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THE APPLICATION OF THERMODYNAMICS TO HETEROGENEOUS EQUILIBRIA.*

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LECTURE I.

THE science of physical chemistry has been developed from two standpoints: That of the kinetic theory, in which the relations between the phenomena discussed are derived by reasoning about the probable mechanism of the reactions; and that of thermodynamics, in which these relations are developed by the application of the two laws which form the basis of this science. These two laws in their simplest form are but the expression of fundamental relationships which are obvious common sense. The first states that when energy is transformed from one manifestation to another, none of it is lost; that all of the energy can be accounted for in one form or another. When coal is burned to heat a boiler to generate steam to run a steam engine to run a dynamo to generate electricity to charge a storage battery, only a small proportion of the energy of the coal becomes stored up in the battery. The rest has not vanished without a trace; we can follow each stage in the process, and see that in

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the boiler room some energy passes off in the stack gases, some by radiation and conduction, and some is delivered to the engine in the steam. Here again we have part of the energy bound in the steam transformed into heat which is transferred to the surroundings by radiation and conduction, part is discharged by the condensed water, and a part is transformed into mechanical work. In the last stage of the process cited, some of the electrical energy is transformed into heat, some does chemical work and is bound by the storage cell. Thus, the energy of the chemical reaction of combustion of the coal has been transformed into heat, mechanical, electrical, and again into chemical energy, and in each stage a balance can be struck showing what has become of all the energy delivered to that stage. The first law of thermodynamics merely states what we are all aware of, that all the energy that is put into a system can be accounted for in some manner, none disappearing.

The second law of thermodynamics is also fundamentally a simple concept. Its general statement has been made in many different forms, such as that heat will not of itself flow from a colder to a warmer body. That is one useful point of view. All expressions emphasize the fundamental fact that heat energy is different from other manifestations of energy; mechanical work can be completely transformed into heat energy, but heat energy cannot be completely transformed into mechanical work; electrical energy can be transformed quantitatively into heat, but a supply of heat energy cannot be transformed into electrical energy without some loss as heat energy. In every transformation of energy a certain amount is dissipated as heat, and practically every operation proceeds in such a manner that as large a proportion of its energy as is possible under the conditions prevailing is dissipated as heat, and, furthermore, the process continues until as large a proportion as is possible under the conditions of pressure, volume, and temperature has been transformed into heat. But this heat energy is not as a rule available for doing work. In some cases, as in the discharged steam from a simple steam engine, there is still some available energy, but ultimately in this case also a proportion of the heat energy is at the temperature of the surroundings and is therefore not available as a source of work. Any process, then, that takes place without

the addition of energy from an outside source goes on in such a manner and to such a condition that as large a proportion as is possible of its energy is "run down," and the "run-down-ness" of the system may be taken as a measure of the extent to which the process has taken place. The two laws may be combined in the statement that in any isolated system, that is, in any combination of substances so placed that energy, either in the form of heat or work, is neither lost nor gained, the energy is constant, but it will tend to get into as run-down a condition as is possible.

This is the qualitative expression of the two laws of thermodynamics, but much more can be gotten out of them by considering their quantitative aspect. Before treating of the quantitative phase, I wish to emphasize the fact that they are true laws, laws which have been tested innumerable times, and always found to be completely true. As long as we introduce no further assumptions, the conclusions reached from thermodynamics are unexceptionable. Whenever we find conclusions deduced by thermodynamic methods that are not in complete accord with facts, such as many of the laws of dilute solutions and the mass law, we must examine the assumptions which have been made. For this reason the thermodynamic methods of attacking chemical problems laid down by Gibbs are, in my opinion, of especial value because of the fact that in all cases we are so close to our fundamental assumptions, and any further assumptions made must be made explicitly. It is not easy to slip in a vitiating assumption unwittingly. There is one point which I wish to mention before proceeding to the quantitative expression of the two laws of thermodynamics, namely, that while I have emphasized the fact that these two laws are primarily the result of experience, at the same time they are deducible from the most general principles of statistical mechanics. Gibbs has shown that they result directly from the application of the laws of probability to a system of particles numerous enough to justify the application of these laws, that is, to a "canonical ensemble." Historically, however, they are empirical experience laws, and for most purposes this is probably the best way in which to consider them.

I have already stated the first law of thermodynamics in the form of the law of conservation of energy; all the energy that is

added to a system can be accounted for as doing work or as stored up in the system. If heat be added to a system, part of it may do work and the rest of it will be stored up in the system as so-called "intrinsic" energy. The intrinsic energy represents the energy bound by the system; it can all be converted into heat by proper change in the experimental conditions. If we add a small amount of heat, dQ, to a system which does work by expansion against an external pressure, p, the first law states that

$$dQ = d\varepsilon + pdV,$$

the heat added, dQ, is partly converted into work, pdV, and the rest increases the intrinsic energy of the system by an amount $d\varepsilon$. In the case of a gas such as H or O, a little less than one-third is converted into work, while in the case of a liquid or solid the proportion is very much less.

The above equation may be written in the form

$$d\varepsilon = dQ - pdV$$

in which the intrinsic energy is expressed as a function of the amount of heat added, dQ, and the volume. The term pdV is is of the form xdX, in which x represents the intensity factor of energy, in this case pressure, and the X represents the quantity factor of energy, in this case, dV. Both intensity and quantity factors are contained in the term dQ, but it is more convenient to have this term also of the form xdX. In the case of heat energy, temperature is the intensity factor analgous to pressure in the preceding instance. The quantity factor, analogous to the volume, is yet to be determined.

In the discussion of the qualitative statement of the second law, it was stated that the energy of any system tended to attain a state of as complete run-down-ness as possible. We are familiar with the fact that a supply of heat energy, say the latent heat of crystallization of a substance, is far more useful for doing work if at a high temperature, say 1000°, than if at a low temperature; the heat energy at room temperature is in a far more run-down condition than when at 1000°. This may be made clearer by considering a volume change taking place in a reaction; the intensity factor is pressure, and the volume change is a certain number of units, say 100 cubic centimetres. If the volume change takes place at a high pressure, say 1000 atmospheres, the work

energy pdV is 100,000 c.c.-atmospheres, or 100 litre-atmospheres. But if the same volume change takes place at one atmosphere pressure, the work energy pdV is only 100 c.c.-atmospheres, or one-tenth of a litre-atmosphere. Now just consider this from another point of view. Suppose at a pressure of 1000 atmospheres we have available a volume change which furnishes us with a supply of work energy which we can measure and find to be equivalent to one litre-atmosphere, and also suppose we are unable for some reason to measure the volume change, but can only measure the pressure and the work energy set free. Obviously, we can calculate the volume change from the relation

$$1 \text{ litre-atmosphere} = 1000 \text{ atmospheres times } x \text{ litres}$$
$$x = 1/1000$$

or one one-thousandth of a litre, or 1 c.c. We cannot calculate either the original or final volume, but this does not interfere with the reality of the volume concept. Similarly, if we have available the same supply of energy, one litre-atmosphere at the pressure of one hundred atmospheres, we can calculate the volume change,

$$x = 1/100 = .01 \text{ litres.}$$

The volume is much larger in this case; the work energy is in a more run-down condition. Similarly, if we have a supply of heat energy available, say from the latent heat of freezing of a substance, and this supply of heat energy, in amount one calorie, is available at 1000°, we can calculate the change in the quantity factor at this temperature just as we did the change in the quantity factor of volume energy at the pressure of 1000 atmospheres. In the case of the heat energy, we have 1 calorie = 1000° times x units of the quantity factor of heat energy, so the change in the quantity factor is 0.001 unit. If the supply of heat energy is available at 100°, the change in the quantity factor is 0.01; the heat energy is in a more run-down condition. This difference in the run-down-ness of the heat energy must be taken into consideration, and the quantity factor of heat energy must express the run-down-ness of the system. By defining the quantity factor as the quantity of heat supplied, dQ, divided by the temperature at which it is available, T, we evidently obtain a quantity which has the desired properties. The case is analogous to that

of the energy expended as work against the pressure, p; the intensity factor in the one case is pressure, in the other case temperature; in the one case the work energy, $dW = pdV$, in the other case the energy is dQ; in the one case the quantity factor is the work energy dW divided by the intensity factor, p, that is $dW/p = dV$; in the other case the quantity factor is the heat energy, dQ, divided by the intensity factor, T, $dQ/T = dS$. The quantity so defined has been termed entropy, and will be designated by S. It may be regarded as a measure of the run-downness of a system. Any isolated system, that is, any system which does not gain or lose energy from its surroundings, will tend to attain to such a condition that its entropy is as great as possible; the condition of isolation implies that during the process the energy must be constant, otherwise there will be heat interchange with the surroundings, and also that the volume must be constant, otherwise there will be work interchange with the surroundings. When the system has reached such a condition that its entropy is a maximum, that is, it is as completely run-down as it is possible for it to be without change of energy or volume, it is in a state of equilibrium. When the entropy is a maximum, change in any of the conditions would result in a decrease in entropy, but our second law states that things do not of themselves go that way.

We now have found the proper substitution for dQ in the equation

$$d\epsilon = dQ - pdV;$$

it is

$$dQ = TdS,$$

in which the temperature, T, is the intensity factor of heat energy, and the entropy change, dS, is the quantity factor of heat energy. Our equation then becomes

$$d\epsilon = TdS - pdV,$$

which is the combined expression for the first and second laws of thermodynamics as usually expressed.

It is unfortunate that in dealing with the really interesting subject of the application of thermodynamics to chemical equilibrium it is necessary to devote so much time to the essentially uninteresting fundamentals of thermodynamics. It would have

been much easier to start in to-day by writing down this equation, but it is usually better to start at the beginning, and I wish to emphasize the fact that in this method of treatment we are never far from the fundamentals. The rest of this lecture will be devoted to the development of the more essentially chemical aspect of the subject, and will clear the way for explicit discussion of actual systems in later lectures. To state concretely the problem before us, we wish to determine the conditions for equilibrium of a mass of matter of various kinds; in chemical problems we deal not with a one-component system such as steam or ammonia, the usual province of thermodynamics in its engineering applications, but with systems of varying degrees of complexity. We wish to determine the conditions of equilibrium of a mass of matter of different kinds, and in order to make it possible to include only such actions as we are desirous of studying, we will assume for the purpose of derivation of our equations that the mass is enclosed in a rigid and fixed envelope, which is impermeable to, and unaltered by, any of the substances enclosed, and perfectly non-conducting to heat. This gives us our isolated system, and it involves no loss in generality. This is evident from the fact that if any mass of matter were in equilibrium it would remain in equilibrium if the whole or any part of it were enclosed in an envelope as supposed. For the purpose of our discussion, we will also exclude the action of gravity, or electrical forces, and of capillarity. These factors do not come into play in the equilibria which I am going to discuss; Gibbs excludes them in his preliminary discussion, but later, one by one, removes these restrictions, and I can do no better than to refer to his classic paper for a discussion of these subjects.

When we apply the combined statement of the first and second laws to a mass of matter of invariable composition, we can express the energy as a function of the entropy and volume:

$$d\epsilon = TdS - pdV.$$

But when the mass consists of several different kinds of matter, each independently variable, such as an aqueous solution, we must include terms to express the change of energy when the quantity of each of these is altered. The terms representing such variation must be of the form xdX, the product of an intensity factor into the change of the quantity factor, and obviously the quantity

factor is the mass of the substance added or subtracted. The intensity factor will be the rate of change of the energy of the mass as the substance is added, other variables being constant.

The intensity factors, pressure and temperature, can be considered in a similar manner. When volume is constant,

$$d\epsilon = T dS,$$

and in this case the intensity factor, temperature, is the rate of increase of energy as entropy is added;

$$d\epsilon/dS = T.$$

Similarly, when the entropy is constant, the intensity factor, pressure, is the rate of increase of energy with increase in volume,

$$d\epsilon/dV = p.$$

In the same manner we can define the intensity factor of chemical energy associated with the mass dm_1 of one component, as the rate of increase of energy with increase of m_1. Denoting this intensity factor of chemical energy by μ, we get

$$d\epsilon/dm_1 = \mu_1.$$

If we are dealing with two independently variable components, such as salt and water, we can write the complete differential of energy, the summation of all the possible ways in which the energy of the system can change, in the form

$$d\epsilon = T dS - p dV + \mu_1 dm_1 + \mu_2 dm_2,$$

in which μ_1 and m_1 refer to water, μ_2 and m_2 to salt. This is a perfectly general expression of the application of the two laws of thermodynamics to any system of two components. It can be extended to include any number of components by the inclusion of a term of the form μdm for each independently variable component. This can be expressed by writing the equation in the form

$$d\epsilon = T dS - p dV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n.$$

It can be regarded as the fundamental equation of chemical thermodynamics, and all the laws of physical chemistry can be derived directly from this equation.

The quantity μ, the intensity factor of chemical energy, requires a few words of explanation. We give the name *chemical*

potential to the quantity μ, and Gibbs defined it in the following words:

"If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered."

The chemical potential has been defined for a unit weight of the substance; for a mol of the substance it is evidently the molecular weight times the quantity so defined, and the molecular chemical potential is identical with the quantity called "partial molar free energy" by Lewis. It is evidently a measure of the strength of the chemical forces which hold the substance in the homogeneous mass in question, say the solution, and subsequently I will show its relation to vapor pressure, in the case of a volatile component.

In our general equation we have terms representing the heat energy, the volume energy, and the chemical energy of each component. In considering the equilibrium relations, the intensity factors of each form of energy are of particular importance because it is necessary for equilibrium that they be uniform throughout the mass. Moreover, this is true whether our system consists only of one homogeneous mass, or whether it consists of several such masses, each uniform in composition and separated from each other by distinct surfaces of discontinuity. Such individually homogeneous parts are termed phases, and when we are considering equilibrium between several phases, it is necessary that the intensity factors, temperature, pressure, and the several potentials, shall not only be uniform in each phase, but also the same for the several phases. This appears to be self-evident; if the temperature is not uniform, it will speedily become uniform by conduction and convection; if the pressure is not uniform, it will become so by mechanical movement; and if the potential for any component is not uniform, it will become so by a re-distribution of that component. I will not go into the proof of this; Gibbs proves it explicitly, showing that it follows as a direct consequence of the application of the second law: The tendency for any system to attain a condition

of as complete run-down-ness as possible, that is, the tendency for the entropy to reach maximum results in uniformity of the intensity factors, temperature, pressure, and chemical potential throughout the mass.

The equation

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

represents the application of the combined laws of thermodynamics to a chemical system composed of several substances, such as water and salt. For direct application to chemical processes, it is usually more convenient to use an equation containing temperature and pressure as expressed variables, instead of entropy and volume, since it is usually these that we control directly. Such an equation can be derived from the preceding without the introduction of any further assumptions, and consequently it also is an expression of the application of the two laws of thermodynamics to chemical systems. The above equation may be regarded as representing the energy of an infinitesimal portion of the given mass, the total energy of the infinitesimal portion, $d\epsilon$, being regarded as the sum of the heat energy, TdS, the volume energy, pdV, and the various chemical energies, μdm, of the infinitesimal portion of the mass. If we add up all such portions we obtain the total energy of the mass; in mathematical language, if we integrate, supposing the quantity of the mass to vary from zero to any finite value, we obtain the expression

$$\epsilon = TS - pV + \mu_1 m_1 + \mu_2 m_2 + \ldots\ldots + \mu_n m_n,$$

which expresses the fact that the total energy of the mass is equal to the sum of the heat energy, the volume energy, and the various chemical energies. If we now differentiate this equation in the most general manner, regarding both temperature and entropy, pressure and volume, and potential and quantity of each component, as independently variable, we get, since the differential of a product of two variables is the sum of each variable into the differential of the other, the equation

$$d\epsilon = TdS + SdT - pdV - Vdp + \mu_1 dm_1 + m_1 d\mu_1 + \mu_2 dm_2 + m_2 d\mu_2 + \ldots\ldots + \mu_n dm_n + m_n d\mu_n.$$

If we compare this with the original equation, we see that the term $d\epsilon$ on the left side of the equation cancels the terms

$$TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

leaving the equation

$$0 = SdT - Vdp + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n,$$

or, as it is more conveniently written,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n.$$

This is Gibbs' equation 97.

It will be observed that this equation contains all the intensity factors, temperature, pressure, and the chemical potentials, as expressed variables, and also states that the algebraic sum of the energy changes associated with changes in these variables is equal to zero. The first equation may be considered as representing the effect of the addition of energy from outside the system; addition of an amount of energy $d\epsilon$ to the system resulted in a re-distribution of this amount of energy as heat, volume, and chemical energy. On the other hand, if a reaction takes place in the system without loss or gain of energy, it results in a change in the temperature, pressure, and the several potentials, the amount of the change in each being given by equation 97.

If we have a system composed of several components in several phases, there will be an equation of the form of 97 for each of the phases, and in each equation the intensity factors are the same, if the phases are in equilibrium. This follows from the second law. In equation 97 there are two more terms than there are components. For each independently variable component there is a term of the form $md\mu$; and if there are n components there will be n terms of this form. In addition, there are in equation 97 two other terms, Vdp and SdT, so there are $n+2$ variables for each phase. If there are two more phases than there are components, there will be $n+2$ equations between the $n+2$ variables, and the system will be completely determined; the equations can be solved and the values of all variables calculated. Such a coincidence of $n+2$ phases is only possible at a given temperature, pressure, and composition of the phases, and is termed an invariant point, and the system is

said to have no degrees of freedom. If there are only $n+1$ phases, there will be $n+1$ equations between the $n+2$ variables, and if we eliminate the n potentials we have an equation between the pressure and temperature, so fixing either of these will determine the condition of the system; the system is univariant, or has one degree of freedom. With only n phases, two more restrictions must be applied, and the system is said to have two degrees of freedom. In the case of a two-component system existing in two phases, we may have any number of different solutions at a variety of temperatures, each with its own pressure, and to determine completely the state of the system we must fix two of these variables. We can fix the composition of the solution and the temperature, and then the pressure is fixed; or we can say the solution has a certain vapor pressure at a certain temperature and this will fix its composition. More generally, if p is the number of phases, n the number of components, and f the number of degrees of freedom,

$$n+2=p+f,$$

and this is the usual statement of the phase rule. This gives us a general relation between the number of components, the number of phases, and the degrees of freedom, but as we shall see later, equation 97 can give us a great deal more information than this about heterogeneous equilibria, that is, about the conditions governing equilibrium between several phases.

The simplest case of heterogeneous equilibrium is that of a one-component system, such as water, coexisting with its own vapor at a series of pressures and temperatures. In this case we have two equations of the form of 97, one for the vapor and one for the liquid, if we denote vapor and liquid by the indices v and l, respectively, these equations are

$$V^v dp = S^v dT + m^v d\mu \qquad \text{and}$$

$$V^l dp = S^l dT + m^l d\mu.$$

It will be remembered, from the derivation of these equations, that the quantities V and S refer to the total volume and total entropy of the mass considered; in this case, where there is only one component, to the total volume and entropy of the m grams

contained in each phase. If we divide each equation through by the mass m, they take the form

$$v^v dp = s^v dT + d\mu$$
$$v^l dp = s^l dT + d\mu,$$

in which the lower case letters are used to denote specific volume and specific entropy, as opposed to the total volume and total entropy, denoted by the capital letters. We can eliminate $d\mu$ between these equations by simple subtraction, giving us

$$(v^v - v^l)\, dp = (s^v - s^l) dT,$$

or

$$dp/dT = (s^v - s^l)/(v^v - v^l).$$

Since $dS = dQ/T$ this reduces to the usual Clausius-Clapeyron equation,

$$dp/dT = dQ/T(v^v - v^l).$$

In the next lecture I will consider the application of this equation to water in more detail, and then apply equation 97 to some systems of two components.

SUMMARY.

To sum up, then, we have seen that the first and second laws of thermodynamics are primarily experience laws, the first of which is the law of conservation of energy, and the second states that energy always tends to become run-down to a less available form. The mathematical expression of the combined laws for a system of constant composition is given by the expression

$$d\epsilon = TdS - pdV,$$

in which TdS represents the heat received by the system, and pdV the work done by the system. But if we consider the system as composed of several separately variable components, the energy must be considered as a function, not only of its volume and entropy, but also of the quantities of the various independently variable components. In this case the differential of the energy may be written

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n,$$

in which m_1, m_2, . . . m_n represent the quantities of each of the n components, and μ_1, μ_2, . . . μ_n quantities called the chemi-

cal potentials, defined as being the amount in which the energy of a homogeneous mass is increased by the addition of an infinitesimal amount of the substance in question, divided by the amount of the substance added. Integration of this equation, supposing the quantity to vary from zero to any finite amount, yields the equation

$$\epsilon = TS - pV + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n$$

and by differentiation of this in the most general manner and comparing the result with the original equation, we get Gibbs' equation 97,

$$V dp = S dT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots + m_n d\mu_n.$$

This is a perfectly general equation between the intensity factors, of which there are, in a system of n components, n chemical potentials, and also the intensity factors, pressure and temperature; $n+2$ in all. If there are $n+2$ phases there will be $n+2$ equations of the form of 97, one for each of the phases, between the $n+2$ variables, and the system will be completely defined. If we call the number of additional restrictions which must be imposed on a system of p phases and n components the number of degrees of freedom, represented by f, we get the usual statement of the phase rule,

$$n + 2 = p + f.$$

Application of equation 97 to the equilibrium between liquid and its vapor gives the equation

$$dp/dT = (s^v - s^l)/(v^w - v^l),$$

in which the quantity factors refer to specific quantities. This is identical with the usual Clausius-Clapeyron equation.

LECTURE 2.

In the previous lecture it was shown that the two laws of thermodynamics, when applied to a system of constant composition, lead to an equation between the energy of a system and its entropy and volume,

$$d\epsilon = T dS - p dV$$

and it was pointed out that the entropy can be considered as the quantity factor of heat energy, temperature being considered as the intensity factor. When the system considered is made of

several independently variable components, the energy is a function not only of the entropy and volume, but also of the masses of the several components, and the complete differential of energy is given by the equation

$$de = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

in which the quantity μ represents the intensity factor of the chemical energy, and the condition of equilibrium is given by equality throughout the system of each of the intensity factors, temperature, pressure, and the several chemical potentials. By integration of this equation and differentiation in the most general manner and comparison with the original, the equation

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n$$

can be obtained. This also is a perfectly general consequence of the first and second laws, and from it the phase rule follows as a necessary consequence. When applied to the equilibrium between water and water vapor, we have two equations of this form, one for the liquid, the other for the vapor, and by elimination of $d\mu$ between the two equations we get an expression for the slope of the pressure-temperature curve,

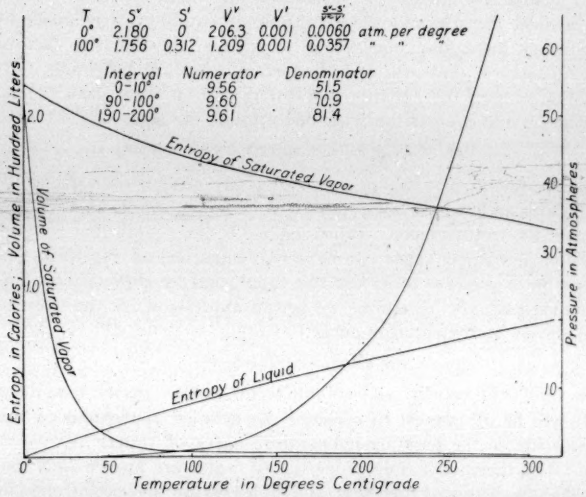
$$dp/dT = (s^v - s^l)/(v^v - v^l),$$

in which the entropy and volume terms denote specific quantities. It will be of interest to consider the detailed application of this equation to the pressure-temperature curve of water.

The thermodynamic properties of water are known to a considerable degree of precision, and tables giving the specific entropy and specific volume of water and steam are in common use by engineers. In such tables it is customary to take the specific entropy of liquid water at zero degrees Centigrade as zero, but since we are always dealing with differences in entropy this is immaterial. Absolute values of entropy are not determinable; to determine absolute values of entropy we would have to know the value of the entropy at absolute zero, and its variation with temperature from the absolute zero up, and we do not possess the necessary data for this. Herein lies one of the reasons for the entropy concept being a difficult one to grasp; we are not able to measure entropy directly as we are able to measure the other quantity factors volume and mass. For practical purposes, however, this is not material, since we are always dealing with entropy

differences. In Fig. 1 are shown plotted the entropy of liquid water and the specific entropy of saturated water vapor from zero to 200° C., the specific volume of water vapor at the saturation pressure in the same temperature range, and the pressure-

FIG. 1.



The one-component system water, showing the change with temperature of the entropy and volume of saturated vapor, of the entropy of liquid in equilibrium with vapor, and of the saturation pressure.

temperature curve of the equilibrium liquid-vapor. Since the slope of the P-T curve is determined by the entropy difference, it is immaterial whether the liquid curve starts at zero degrees or at some other value, since the entropy of the vapor would differ from that of the liquid by the entropy of vaporization, that is, the heat of vaporization divided by the absolute temperature, and any correction added to the liquid would also be added to the vapor. In the case of the volume, only the specific volume of the vapor is plotted, as that of the liquid is so small that it cannot be shown on the scale of the diagram. Let us now consider some actual values.

At zero degrees Centigrade, if the entropy of the liquid is zero, that of the vapor is 2.18 calories. The specific volume of water vapor in equilibrium with liquid at zero degrees is 206 litres per gram; it is evident that the volume of the liquid, 1 c.c., is negligible in comparison. In the equation

$$dp/dT = (s^v - s^l)/(v^v - v^l)$$

the terms must all be of the same kind; if the slope of the P-T curve is given in atmosphere per degree, and the volume in litres, the entropy must be expressed in litre-atmospheres instead of in calories. The factor for this conversion is 0.0413; inserting the above values in the equation, we get

$$dp/dT = (2.180 \times 0.0413)/206 = 0.00044 \text{ atm. per degree};$$

the corresponding experimental value is the same. At 50° the values are

$$\frac{dp}{dT} = \frac{(1.928-0.168)(0.0413)}{(12.02-0.001)} = 0.0060.$$

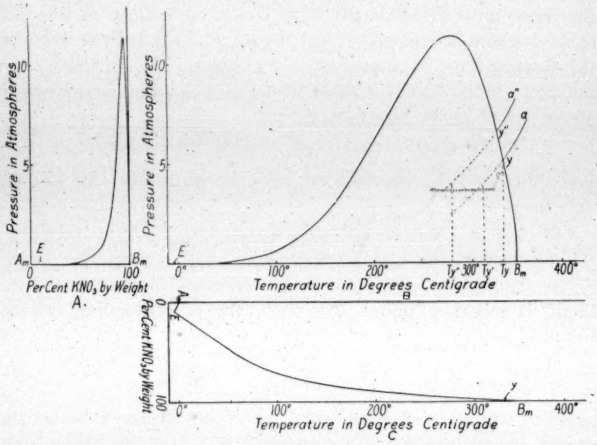
Again the experimental value is the same, and the volume of the liquid is still negligible. At 100°, the corresponding quantities are

$$\frac{dp}{dT} = \frac{(1.756-0.312)(0.0413)}{(1.209-0.001)} = 0.0357,$$

agreeing exactly with experiment. In this case the value of the specific volume of the liquid amounts to less than one-tenth of one per cent. It is evident that the value of dp/dT is increasing with increasing temperature, and the explanation is evident from an inspection of the entropy and volume curves. As the temperature is increased the entropy of the vapor diminishes, that of the liquid increases, hence the difference decreases as the temperature increases. The numerator, the entropy of vaporization, is therefore diminishing, but its decrease is more than offset by the decrease in the denominator taking place at the same time as the result of the increasing vapor pressure increasing the density of the vapor, hence decreasing its specific volume. In the interval from zero to 10° the numerator decreases to 95.6 per cent. of its value at zero, while the denominator decreases to only 51.5 per cent. of its value at zero. The difference does not remain so marked, but for the interval 90–100° the values are 96 per cent.

and 70.9 per cent., respectively, and for the interval 190–200°, 96.1 per cent. and 81.4 per cent., respectively. Application of equation 97 to the univariant equilibrium liquid-vapor in the one-component system water shows us that not only does the pressure increase with increasing temperature, but the rate of

FIG. 2.



The binary system water-potassium nitrate. Projections of the solid pressure-temperature-concentration model on the P-X, P-T and T-X planes.

increase also increases. The P-T curve is accordingly concave upward. We will now consider the case of a simple binary system, choosing the system water-KNO_3 as illustration (Fig. 2).

The system H_2O-KNO_3 does not show liquid immiscibility, nor are solid hydrates formed, so there are four possible phases in the system; one vapor phase, one liquid phase and two solids, solid ice and solid KNO_3. Coexistence of four phases in a two-component system gives us four equations of the type of 97 between the four unknowns, pressure, temperature, and the two chemical potentials, so the system is completely determined. The four phases can only coexist at one temperature and one pressure, that is, at the invariant point, often called the cryohydrate, when

one component is water. The invariant point can be considered as the intersection of four curves representing univariant equilibria, each of which equilibria will contain three of the phases which coexisted at the invariant point. We can have the four combinations ice-solution-vapor, ice-potassium-nitrate-vapor, ice-potassium-nitrate-solution, and potassium-nitrate-solution-vapor. We will consider each of these curves in detail, starting with the last, the solubility curve of potassium nitrate in water.

In the univariant equilibrium potassium-nitrate-solution-vapor there is only one phase of variable composition, the solution. Since potassium nitrate is not volatile at temperatures we are considering, the vapor phase is pure water; since potassium nitrate forms neither hydrates nor solid solutions with water, the solid phase is pure potassium nitrate. Let us now apply equation 97 to this univariant equilibrium. In the derivation of equation 97,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2$$

for a two-component system, we have expressed composition as the total mass m_1 and m_2 of the substances present, and volume and entropy as total volume and total entropy. For some purposes this is the most convenient form, but for our present discussion it is more convenient to express composition as weight per cent. potassium nitrate. Since we have $m_1 + m_2$ grams of the two components water and potassium nitrate, respectively, if we divide through by $m_1 + m_2$ we shall get

$$\frac{V}{m_1 + m_2} dp = \frac{S}{m_1 + m_2} dT + \frac{m_1}{m_1 + m_2} d\mu_1 + \frac{m_2}{m_1 + m_2} d\mu_2 .$$

The coefficient of the first term, the total volume divided by the total number of grams of material, is evidently the specific volume of the phase. Similarly, the coefficient of the second term is the specific entropy. The fractions

$$\frac{m_1}{m_1 + m_2} \text{ and } \frac{m_2}{m_1 + m_2}$$

are the weight fractions of the components H_2O and KNO_3, respectively, and if we represent the weight fraction of KNO_3 by x, that of H_2O will be $(1-x)$. The equation now is

$$vdp = sdT + (1-x)\, d\mu_1 + x d\mu_2,$$

in which v and s are specific volume and specific entropy. We will have three such equations, one for the vapor, denoted by

the exponent v, one for the liquid, denoted by the exponent l, and one for the solid, denoted by the exponent s. From these equations we may eliminate $d\mu_1$ and $d\mu_2$ by the usual methods of cross-multiplication, giving the equation

$$\frac{dp}{dT} = \frac{(s^v - s^l) - \frac{x^v - x}{x^s - x^l}(s - s^l)}{(v^v - v^l) - \frac{x^v - x^l}{x^s - x^l}(v^s - v^l)}.$$

At the cryohydrate the weight fraction KNO_3 is 0.021; since the vapor is pure water, its weight fraction KNO_3 is zero, and that of the solid phase is unity. Substituting these values, we get

$$\frac{dp}{dT} = \frac{(s^v - s^l) + \frac{.021}{.979}(s^s - s^l)}{(v^v - v^l) + \frac{.021}{.979}(v^s - v^l)}.$$

The coefficient of the second term in both numerator and denominator is a fractional coefficient. Without an actual determination of the entropy of any phase, certain definite conclusions can be drawn. In the numerator, we have the entropy differences: Vapor-liquid, a positive quantity, and solid-liquid, a negative quantity. The former is always several times the latter; in the case of this dilute solution their ratio is probably not very different from the ratio of the entropy of vaporization of water to the entropy of fusion of KNO_3, of the order of magnitude of 20 to 1. The first term predominates, and the numerator is a positive quantity of the order of magnitude of the entropy of vaporization of water at zero degrees, or a little less than 2.18. In the denominator the term affected by the fractional exponent, the difference in specific volume of liquid and solid is negative and is itself very small. The first term, the volume difference vapor-liquid, is comparatively enormous; at the cryohydrate temperature and pressure it is even larger than the volume difference in pure water at its freezing point, 206 litres per gram. The slope of the pressure-temperature curve is at the beginning close to that of pure water; that of pure water is concave upward, due to the denominator decreasing in value more rapidly than the numerator, and the same is true in this case. In fact, the pressure-temperature curve of all systems containing a volatile component at low pressure will show a similar initial upward concavity, due to the rapid decrease in the specific volume of the vapor phase with increasing pressure.

As the temperature is raised, the fraction KNO_3 in the liquid increases, while the composition of the other phases remains the same. The specific entropy of the vapor continually decreases; that of the solid increases, as does that of the liquid. The first term in the numerator consequently decreases, the second increases, and the coefficient of the second term also increases; since the first term is positive, while the second is negative, the numerator is a continually decreasing positive quantity. The denominator is decreasing at a progressively slower rate. As the temperature is raised these effects continue, until a temperature is reached at which the rate of decrease of the numerator becomes equal to that of the denominator, and the curve has a point of inflection, after which it is no longer concave upward, but is concave downward; the vapor pressure of the saturated solution is still increasing with the temperature, but at a diminishing rate. The temperature of this point of inflection is approximately 145°, and the pressure is about 2.5 atmospheres.

The determination of the solubility curve of KNO_3 in H_2O is a simple matter at temperatures below 100°. As long as the vapor pressure remains less than one atmosphere, we can shake up solid and liquid in a thermostat until equilibrium is reached, suck out a sample of the supernatant liquid through a filter, and determine the composition by analysis. After the pressure has exceeded one atmosphere, other methods must be employed. Of course, if a mixture containing an excess of KNO_3 is heated in an open vessel, when the vapor pressure reaches one atmosphere the solution will begin to boil, and will evaporate to dryness. But if the mixture be heated in a closed tube, from which the water cannot evaporate, the solubility curve will be continuous until the mixture is entirely liquid; the temperature at which the saturated solution boils at a pressure of one atmosphere is not a significant point on the solubility curve. From this point of view there is no distinction between a solubility curve and a melting-point curve, and the curve EB_m can be regarded either as the solubility curve of KNO_3 in H_2O or as the melting-point curve of H_2O-KNO_3 mixtures. The first to realize this fact was Guthrie in 1886, and the system H_2O-KNO_3 was one of those which he studied. He sealed mixtures in closed tubes and observed the temperature at

which the crystals disappeared. In a later lecture I will describe another method for studying solubility curves at high temperatures which can be applied over a much greater range of pressure and temperature and to a greater variety of substances than can this simple closed tube method.

As the temperature is raised past the point of inflection of the P-T curve, the KNO_3 content of the liquid increases and the coefficient of the second term in the numerator increases correspondingly. At 115°, the boiling point of the saturation solution, the ratio $x^l/(1-x^l)$ is about 2.5; at the point of inflection, about 4. As this coefficient continues to increase, the numerator decreases more and more rapidly, and the value of dp/dT decreases; but, as it is still positive, the pressure continues to increase with temperature. With a little further increase in temperature, the ratio $x^l/(1-x^l)$ becomes such that the entire second term equals the first term, and the difference is zero; the numerator is now zero, so dp/dT is zero, and the curve has a horizontal tangent. Since at this point

$$(s^v - s^l) + x^l/(1-x^l)\ [s^s - s^l] = 0$$

it follows that

$$x^l/(1-x^l) = -(s^v - s^l)/(s^s - s^l).$$

The ratio of the entropy difference vapor-liquid to the entropy difference solid-liquid is equal to the ratio of KNO_3 to water in the saturated solution; the saturated solution at this point contains about 95.7 per cent. KNO_3, so this ratio is approximately 95.7/4.3, or 22. The entropy of the water vapor at this temperature and pressure can be obtained from steam tables, that of KNO_3 from specific heat data, and the entropy of the liquid can accordingly be calculated. It should be remembered that we are here dealing with entropy differences, not absolute entropy, and when we take off the entropy of the steam from a steam table the assumption is made that the entropy of liquid water at its freezing point is zero. This does not diminish the usefulness of the steam tables, and neither does it interfere with the application to heterogeneous equilibria, but we must keep straight in our minds about it.

The point of maximum pressure is found at a KNO_3 content

of about 95.7 per cent., a temperature of about 275°, and a pressure of about 11 atmospheres. Our equation is

$$\frac{dp}{dT} = \frac{s^v - s^l + \frac{0.957}{1 - .957}(s^s - s^l)}{v^v - v^l + \frac{0.957}{.043}(v^s - v^l)}$$

and the numerator is zero because the negative entropy difference solid-liquid, multiplied by the ratio $x^l/1-x^l$ is equal to the positive entropy difference vapor-liquid. On further increase in temperature x^l continues to increase, the negative second term becomes larger than the positive first term, and the numerator becomes negative. The denominator is still positive, so the P-T curve has a negative slope; pressure decreases with increasing temperature. On further increase in temperature, the numerator continues to become more strongly negative, until at the melting point of pure KNO_3 it is the entropy difference solid-liquid for KNO_3.

The changes which have been taking place in the denominator will now be considered. The specific volume of the vapor phase at all points is much larger than that of any other phases, its smallest value at the maximum pressure being about 100 c.c. As the pressure decreases from this point, the specific volume of the vapor increases; the effect of this is merely to alter the rate of decrease of pressure which takes place from this point. But as the liquid phase approaches KNO_3 in composition, the amount of water becoming very small, the second term in the denominator becomes of importance. The specific volume difference between fused and solid KNO_3 is but a few tenths of a cubic centimetre; when the water content is only 0.1 per cent., the negative volume difference solid-liquid is multiplied by the ratio 999/1, and at 0.01 per cent. water, by 10,000. At some small water content the large positive volume difference vapor-liquid is equalled by the much smaller negative volume difference solid-liquid, and the denominator becomes zero, the slope of the P-T curve, dp/dT, infinite. At this point the curve is vertical; on further increase in temperature the curve again has a positive slope. In a system of the type H_2O-KNO_3 the experimental realization of this portion of the curve would be extremely difficult and we will not consider

it further at present, except to point out that at a zero water content the equation becomes

$$\frac{dp}{dT} = \frac{s^s - s^l}{v^s - v^l},$$

the melting-point curve of pure KNO_3. The P-T curve of the saturated solutions is therefore tangent at its end to the melting-point curve of KNO_3, the curve showing the change in melting point of potassium nitrate with pressure. This type of equilibrium will be considered later.

We have seen that a melting-point or solubility curve of the system H_2O-KNO_3 extends from the cryohydrate E to the melting point of pure KNO_3, and have followed the change in vapor pressure with composition in detail. We have therefore correlated the temperature-composition or solubility curve with the pressure-temperature curve. One curve gives the change in composition of the liquid in equilibrium with solid and vapor with the temperature, the other gives the change in vapor pressure of the saturated solution with temperature. One other pair of the three variables, composition of the liquid, temperature, and pressure, can be considered, namely, the change in vapor pressure of the saturated solution with composition. This is the pressure-composition curve; from it we see that the vapor pressure at first increases with increasing water content of the saturated solutions, reaches a maximum at a small H_2O content, then decreases rapidly with further diminution of the water content, until at its end-point at pure KNO_3 the vapor pressure is that of the triple point of KNO_3. We are all familiar with the fact that as the water content of the saturated solution increases with increasing temperature the vapor pressure increases, until at the boiling point of the solution the pressure of the atmosphere is reached. But there are two saturated solutions whose vapor pressure is one atmosphere; one has a water content of 29 per cent., the other of only one per cent. At the first boiling point, addition of heat causes the solution to evaporate, liquid changing into solid and vapor. At the boiling point at higher temperature, called by Roozeboom, who discovered it, the second boiling point, the solution boils on cooling. At the second boiling point, the liquid changes into solid and vapor with evolution of heat. If a melt of KNO_3,

saturated at its melting point with water, be quickly cooled, it will be seen to boil suddenly and violently, and at the same time to solidify. This second boiling point has been observed in many systems, including silicate systems at high temperatures.

We have considered but one of the four univariant equilibria which proceed from the invariant point, the univariant equilibrium solid KNO_3-solution-vapor. The system ice-solution-vapor is a second equilibrium in which we have both liquid and vapor, and in this case solid and vapor have the same composition. Our equation becomes:

$$\frac{dp}{dT} = \frac{s^v - s^l - \frac{x^v - x^l}{x^s - x^l}(s^s - s^l)}{v^v - v^l - \frac{x^v - x^l}{x^s - x^l}(v^s - v^l)}$$

and, since $x^v = x^s = 0$,

$$\frac{dp}{dT} = \frac{s^v - s^l - \frac{0 - x^l}{0 - x^l}(s^s - s^l)}{v^v - v^l - \frac{0 - x^l}{0 - x^l}(v^s - v^l)}.$$

Cancelling, this becomes

$$\frac{dp}{dT} = \frac{s^v - s^s}{v^v - v^s}.$$

But this is the equation of the vapor-pressure curve of ice; all terms relating to the liquid have disappeared. This is a general relation; whenever any two phases in a binary system have the same composition the pressure-temperature relations become those of these two phases, without reference to the composition of the other phase present.

The preceding univariant equilibria have been formed by the disappearance of ice or of KNO_3, respectively; two more can be obtained, by the disappearance of liquid or of vapor. In case the liquid disappears, we have left ice, KNO_3, and water vapor, and the P-T curve of this equilibrium will coincide with the vapor-pressure curve of ice, and from the invariant point will go to lower pressure and lower temperature. In case the vapor disappears we have the condensed system ice-KNO_3-liquid, and the curve gives the change in eutectic composition with pressure. The equation of this curve is

$$\frac{dp}{dT} = \frac{s^{ice} - s^l - \frac{x^{ice} - x^l}{x^{KNO_3} - x^l}(s^{KNO_3} - s^l)}{v^{ice} - v^l - \frac{x^{ice} - x^l}{x^{KNO_3} - x^l}(v^{KNO_3} - v^l)}$$

and since $x^{ice} = 0$, $x^{KNO_3} = 1$, and $x^l = .021$, this becomes

$$\frac{dp}{dT} = \frac{s^{ice} - s^l + \frac{.021}{.979}(s^{KNO_3} - s^l)}{v^{ice} - v^l + \frac{.021}{.979}(v^{KNO_3} - v^l)}.$$

Here again the entropy and volume changes of the water are the predominating factors; since the entropy difference is positive and the volume difference, in the exceptional case of water, negative, the P-T curve of this equilibrium has a negative slope. But in this case, as in all condensed systems, the slope is very steep; the numerator is of the order of magnitude of 0.3 cal, or 0.012 litre-atmospheres; the denominator is of the order of magnitude of 0.1 c.c., or 0.0001 litres. The value of dp/dT is thus about $-0.012/0.0001$, or 120 atmospheres per degree; the curve will be almost vertical. In other words, pressure as a rule has but little effect on the equilibrium temperature and composition, as compared with temperature.

We have considered the application of equation 97 to the simplest type of system, that in which there is but one phase of variable composition, and no compounds are formed. It will be of interest to see what additional complications are introduced by the formation of compounds, and as illustration the system H_2O-$CaCl_2$ will be chosen.

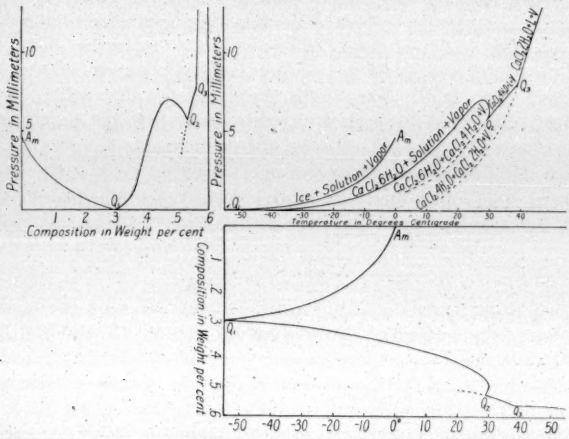
The invariant point ice-$CaCl_2.6H_2O$-solution-vapor is at $-55°$, and the pressure is but a fraction of a millimetre. The compound $CaCl_2.6H_2O$ contains 50.66 per cent. $CaCl_2$, and the cryohydrate solution, 29.8 per cent. The equation of the pressure-temperature curve of the solutions saturated with $CaCl_2.6H_2O$ is

$$\frac{dp}{dT} = \frac{s^v - s^l + \frac{x^l}{.5066 - x^l}(s^s - s^l)}{v_v - v^l + \frac{x^l}{.5066 - x^l}(v^s - v^l)}.$$

As in the preceding case the volume change of the water vapor is the dominating factor at low temperatures, causing the curve to be concave upward (Fig. 3). As the temperature is raised the

fractional coefficient of the second term becomes of increasing importance, as before, and again a point of inflection of the P-T curve is reached at 18°; the solution at this temperature contains 42 per cent. $CaCl_2$, so the coefficient of the second term is now

FIG. 3.



The binary system water-calcium chloride. Projections of the solid pressure-temperature-concentration model on the P-X, P-T, and T-X planes.

0.42/0.5066–0.42, or about 4.2. The curvature falls off rapidly with increase in the $CaCl_2$ content, and becomes zero at 28° and 48.5 per cent. $CaCl_2$. Since at this point

$$\frac{x^l}{.5066 - x^l} = \frac{s^v - s^l}{s^s - s^l}$$

the ratio of the entropy of vaporization to the entropy of solution is 0.485/0.506–0.885, or about 23 to 1. This is approximately the same ratio as was found at the point of maximum pressure in the system H_2O-KNO_3. With further increase in the $CaCl_2$ content the slope of the P-T curve becomes negative, and the pressure falls with increasing temperature.

It will be remembered that in the discussion of the preceding system it was stated that when the liquid phase was very close in

composition to the solid phase, the coefficient of the second term would become large enough for the small negative volume difference solid-liquid, multiplied by the large coefficient, to equal the very much larger and positive volume difference vapor-liquid, but that the effect would be difficult to detect in such a system. When that is the case, the denominator becomes zero, the P-T curve has a vertical tangent, hence a point of maximum temperature. This is shown clearly in this system. On further increase in the $CaCl_2$ content of the solution, a maximum temperature is found, after which both temperature and pressure fall. Two effects take place very close together here; first the liquid approaches the solid so closely that the denominator becomes zero, then the two compositions become identical. When the two phases solid-liquid have the same composition, the equation of the P-T curve becomes

$$\frac{dp}{dT} = \frac{s^s - s^l}{v^s - v^l}$$

which is the equation of the melting-point curve of the hexahydrate; the condensed system liquid $CaCl_2.6H_2O$-solid $CaCl_2.6H_2O$ is one of the great majority of substances that expand on melting; both the specific entropy and the specific volume of the liquid are greater than those of the solid phase. This melting point of the hydrate is called the "minimum melting point" because it is the lowest temperature at which solid and liquid of the same composition can exist together in equilibrium; a whole series of such melting points can be obtained at higher pressures in the absence of vapor, along the melting-point curve of the hydrate, the curve of the condensed system liquid-solid. It should be pointed out that this minimum melting point is not at the point of maximum temperature, but at a lower temperature. The point of maximum temperature is found at such a salt content that the denominator becomes zero, as previously stated, while the minimum melting point lies at a slightly higher salt content, and a lower temperature and pressure. In a system containing a volatile component the point of maximum temperature is not at the composition of the compound, as is the case in systems of non-volatile components or in condensed systems, but at a composition slightly displaced toward the volatile component.

In the case of $CaCl_2.6H_2O$ the difference is very small, and the two points have never been separated, but at higher temperatures and pressures the difference is no longer negligible.

After the minimum melting point has been passed, the coefficient of the second term in the denominator becomes negative, so that in both numerator and denominator the second term, the entropy and volume differences solid-liquid, in themselves negative, are multiplied by a negative coefficient, hence the second term in both becomes positive, and is to be added to the positive first terms. The slope of the P-T curve is then positive, and remains so until the invariant point $CaCl_2.6H_2O$-$CaCl_2.4H_2O$-solution-vapor is reached, at which a new solid phase, calcium chloride tetrahydrate, makes its appearance. The series of P-T curves which proceed from this invariant point when different phases disappear will be considered in the next lecture, as they present some novel features.

SUMMARY.

To sum up, we have considered in detail the application of equation 97 of Gibbs, which is itself a perfectly general expression of the two laws of thermodynamics, to the system water, and to the binary systems H_2O-KNO_3 and H_2O-$CaCl_2$. In the unary system water we found that the equilibrium vapor-liquid took place at a series of corresponding temperatures and pressures, and that the slope of the pressure-temperature curve at any point was determined by the entropy and volume differences between the two phases. The P-T curve of water is concave upward. In the system H_2O-KNO_3 we considered the four univariant equilibria which can be formed from the invariant equilibrium by disappearance of each of the four phases singly. Of these, two represented coexistence of a solid phase with solution and vapor; in that one in which ice is in equilibrium with solution and vapor, the composition changes from pure ice to the cryohydrate solution. In this equilibrium the pressure is the same as the vapor pressure of ice at the same temperature; the solution, while its composition also changes, is without influence on the pressure-temperature relations of the two remaining phases, ice and vapor. This is in consequence of a general relation, according to which in any equilibrium in which the composition of two phases becomes identical the terms relating to the remaining phase drop out of the equation

for the P-T curve. The other univariant equilibrium, the univariant system KNO_3-solution-vapor, is the usual solubility curve of KNO_3 in water, along which the change in composition of the liquid is continuous from the cryohydrate to pure KNO_3. The solubility and the fusion curve are the same, and the circumstance that above the boiling point of water pressure is required to retain the water in the system is without significance in the general relationships involved. The pressure in this system at first increases with temperature, and the pressure-temperature curve is at first concave upward, due to the preponderating effect of the water. At higher temperatures it becomes concave downward, then has a horizontal tangent, then the pressure decreases with increasing temperature, and we have seen that these changes in temperature, pressure and composition are determined by the variations in the quantities in equation 97. The other two univariant equilibria which proceed from the cryohydrate are that of the condensed system ice-solution-KNO_3, which has a steep slope, and that of the system ice-vapor-KNO_3, the P-T curve of which is identical with that of ice, because of the fact that ice and vapor have the same composition. Equation 97 has also been applied to the solubility curve of $CaCl_2.6H_2O$, and the changes in composition, temperature, and pressure correlated by its aid. In this case both the temperature and the pressure have maximum values, both maxima being at a higher water content than that of the compound; and after the solution has become richer in $CaCl_2$ than the hexahydrate both temperature and pressure fall until another phase appears.

LECTURE 3.

In the preceding lectures it has been shown that application of the two laws of thermodynamics to a system composed of several independently variable components leads to the equation

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n,$$

in which ϵ is the total energy, dS, dV, dm_1, dm_2, . . . dm_n are the changes in the quantity factors, total entropy, the quantity factor of heat energy, total volume, and the quantities of the several components. The temperature, pressure, and the chemical potentials (T, p, and μ_1, μ_2, . . . μ_n) are the intensity factors of the heat, volume, and chemical energies, respectively.

From this equation, by integration and differentiation is obtained Gibbs' equation 97,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n,$$

which is also a general deduction from the two laws. Applied to a two-component system, and expressing composition as weight fraction of one component, the component of lesser volatility, the equation becomes

$$vdp = sdT + (1 + x)d\mu_1 + xd\mu_2.$$

The phase rule in its usual form is a direct consequence of this equation, and by its aid we are able to follow the changes in composition, pressure and temperature in detail, as was shown in the case of the unary system water, the binary system H_2O-KNO_3, and the binary system H_2O-$CaCl_2$. In the latter system we followed the solubility curve of the hexahydrate to the invariant point at which the tetrahydrate appears.

At this invariant point (Fig. 3) we have the four phases hexahydrate-tetrahydrate-solution-vapor, and from this invariant point four univariant equilibria are obtained by the disappearance of each, separately, of these four phases. If the liquid phase disappears we have the three phases hexahydrate-tetrahydrate-vapor; since all of these phases are of constant composition the pressure is a function of the temperature only; there is no concomitant change in composition of one of the phases. Our equation becomes

$$\frac{dp}{dT} = \frac{s^v - s^t - \frac{x^v - x^t}{x^h - x^t}(s^h - s^t)}{v^v - v^t - \frac{x^v - x^t}{x^h - x^t}(v^h - v^t)}$$; in which the exponents

h and t represent the hexahydrate and the tetrahydrate, respectively. Substituting the numerical values of x^v, $x^{\text{tetrahydrate}}$ and $x^{\text{hexahydrate}}$, 0, 0.6063, and 0.5066, respectively, gives the value of 6.06 as the constant coefficient of the second term. The equation now becomes

$$\frac{dp}{dT} = \frac{(s^v - s^t) - 6.06\,(s^h - s^t)}{(v^v - v^t) - 6.06\,(v^h - v^t)}.$$

The numerator of this is always positive; the entropy difference hexahydrate-tetrahydrate is negative, since the decomposition of hexahydrate into tetrahydrate and solution, to be considered later, absorbs heat, and this negative term is multiplied by a negative

coefficient, making the two terms in the numerator both positive. The denominator is large and positive, because of the very large specific volume of the vapor. The value of dp/dT is consequently positive, and the pressure increases with the temperature, as is the case with the dissociation pressure of the hexahydrate. It is to be observed that this equilibrium requires the presence of both solid phases hexahydrate and tetrahydrate, which, together with the vapor, make three phases, hence three equations. The common name, dissociation-pressure curve of the hexahydrate, in this sense, is misleading; the equilibrium is the univariant equilibrium between all three phases. The invariant point is the high temperature termination of the stable portion of this curve; when a mixture of these two solids, together with vapor, is heated, at the invariant point some solution is formed; some of the solid melts to form the eutectic liquid.

A second univariant equilibrium is that formed by the disappearance of vapor. This is the condensed system composed of the two hydrates and the eutectic liquid; the composition of the eutectic liquid and the eutectic temperature both change as the pressure is increased, but the change is small, and will not be considered further.

Two univariant equilibria between solid, liquid and vapor can be formed, the solubility curves of the hexahydrate and the tetrahydrate. The first of these was considered in the last lecture; from this invariant point both temperature and pressure increase with increase in water content of the solution, and the hexahydrate has a definite melting point. At the minimum melting point solid hexahydrate melts to form a liquid of the same composition; this is called a congruent melting point.

The other equilibrium between solid, liquid and vapor is the solubility curve of the tetrahydrate. Application of equation 97 to this brings out no novel features; temperature and pressure both increase as the solution becomes richer in $CaCl_2$, and this portion of the P-T curve is concave downward over its entire course. It differs from the preceding, however, because of the circumstances that, before the point at which the P-T curve has a horizontal tangent, a new solid phase appears, calcium chloride dihydrate. This gives rise to another invariant point, at which the four phases are tetrahydrate, dihydrate, solution and vapor. In the case of the hexahydrate the invariant solution was richer

in $CaCl_2$ than the compound disappearing, the solution was a eutectic, and the compound had a congruent melting point. The solution at this invariant point contains 56.4 per cent. $CaCl_2$, while the tetrahydrate contains 60.6 per cent. $CaCl_2$. Substitution of these values in our equation gives

$$\frac{dp}{dT} = \frac{(s^v - s^l) + \frac{.564}{.606 - .564}(s^s - s^l)}{v^v - v^l + 13.4\,(v^s - v^l)};$$

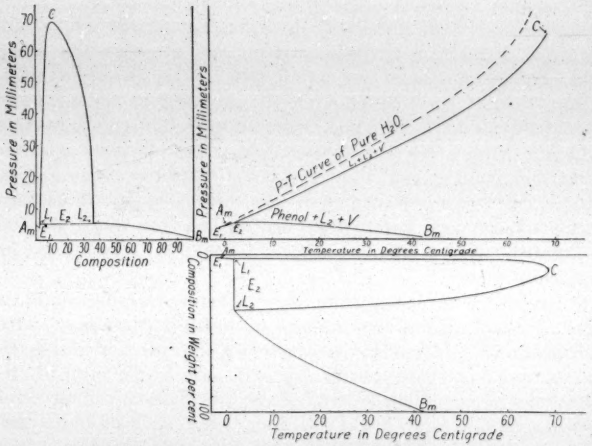
the positive entropy of vaporization is larger than the negative entropy of fusion multiplied by its coefficient, dp/dT is still positive, and both temperature and pressure are increasing along the solubility curve of the tetrahydrate at the invariant point. This solubility curve differs from the preceding in that solid and liquid do not have the same composition at any point; calcium chloride tetrahydrate has an incongruent melting point, and the invariant point is not a eutectic but a transition point. Pure hexahydrate, when heated, melts to form a liquid of its own composition; pure tetrahydrate decomposes into dihydrate and saturated solution of the composition of the solution at the invariant point.

From this invariant point three other univariant equilibria can be obtained, but they require no detailed discussion. One of them is the condensed system, whose P-T curve is almost vertical; a second is the dissociation-pressure curve of the tetrahydrate, the univariant equilibrium tetrahydrate-dihydrate-vapor; the third is the solubility curve of the dihydrate. The application of equation 97 to this equilibrium would present no new features.

The preceding illustrations have been chosen to illustrate the way in which equation 97 of Gibbs, the equation from which the phase rule was derived, can give us definite information as to the equilibrium relations in heterogeneous systems, and phase-rule studies pursued in this manner are capable of yielding much information as to the behavior of unknown systems. The cases chosen have all been simple; complications resulting from several of the phases having a variable composition have not been introduced. The vapor phase might be of variable composition; in this case x^v in our equations would no longer be zero, but would change with temperature and composition of the liquid phase. A solid phase might be of variable composition; in this case solid solution is

formed, but the complications introduced are not as serious as they appear at first sight, and with the aid of equation 97 it is not difficult to fix the equilibrium relations. Also, there might be two liquid layers, both of variable composition; this case is of considerable interest, and it seems to me the usual treatment is needlessly obscure, so I will choose a system in which two liquid layers are formed, as a further example of the method of applying equation 97 to the problem of heterogeneous equilibrium.

FIG. 4.



The binary system water-phenol. Projections of the solid pressure-temperature-concentration model on the P-X, P-T, and T-X planes.

As an example of a system in which two liquid layers are formed, I have taken the system water-phenol, and in the discussion I will omit the formation of the compound that is formed between the two; this compound is not readily formed, and the equilibria between water and phenol in which the compound is not formed are the more easily obtained. The invariant point at which both ice and phenol can exist, together with solution and vapor, is at $-1.2°$ (Fig. 4), and a small concentration of phenol, less than 1 per cent. As the temperature is raised above this point, the solubility of phenol increases slightly, until at $1.7°$ the saturated solution contains about 1.8 per cent. phenol. At this

temperature the solid phenol in equilibrium with the solution melts, taking up water, and forming a second liquid layer. We have then four phases, solid phenol, a liquid containing 1.8 per cent. phenol, a second liquid, immiscible with the first, and containing about 36 per cent. of phenol, and a vapor phase, containing so small an amount of phenol that we may consider it as pure water. Four univariant equilibria proceed from this invariant point. The equilibrium solid phenol-solution-vapor, the solubility curve of solid phenol; and the equilibrium solid phenol-two liquids, a condensed system giving the change in the composition of the two layers in equilibrium with solid with pressure, present no new features, and will not be considered. The equilibrium between vapor, the water-rich liquid, and the phenol-rich liquid is of greater interest. At the invariant point, our equation becomes

$$\frac{dp}{dT} = \frac{s^v - s^{l_1} - \frac{x^v - x^{l_1}}{x^{l_2} - x^{l_1}}(s^{l_2} - s^{l_1})}{v^v - v^{l_1} - \frac{x^v - x^{l_1}}{x^{l_2} - x^{l_1}}(v^{l_2} - v^{l_1})};$$

substituting the values 0, 0.018 and 0.36 for the composition of the vapor, the water-rich liquid and the phenol-rich liquid, respectively, gives us

$$\frac{dp}{dT} = \frac{(s^v - s^{l_1}) + \frac{.018}{.36 - .018}(s^{l_2} - s^{l_1})}{(v^v - v^{l_1}) + .053(v^{l_2} - v^{l_1})}$$

and in this case also the entropy and volume of the water is the dominating factor. The P-T curve accordingly is concave upward. As the temperature is increased, the two liquids approach each other in composition, the water-rich layer changing less than the phenol-rich layer. But at the same time their specific entropies and specific volumes approach each other, since both are liquids, composed of the same components, and increasingly close to each other in composition. For this reason the increasing value of the coefficient of the second term is offset by the decrease in the second term itself, and no maximum pressure is found. Finally, the two phases become identical in composition and properties. At the same time that the difference in composition becomes zero the difference in entropy and the difference in volume become zero, and the equation becomes indeterminate. This is as should be expected; the three-phase system was univariant because there

were three equations between the three quantities—pressure, temperature, and composition. When the two liquid phases become identical, not only in composition but also in properties, there are no longer three phases, but two only, and the system is no longer univariant but divariant. In the case of calcium-chloride-hexahydrate, when the liquid and solid phases had the same composition at the minimum melting point, there was still an entropy difference, since it takes heat to melt a solid, and a volume difference; in this case all distinction between the phases disappears, and there are but two phases, liquid and vapor. At the temperature at which the two liquids merge into one another there may be not only the critical solution, but also any other mixture of liquid phenol and water; the composition of the solution or the vapor pressure must be fixed in order to completely determine the system.

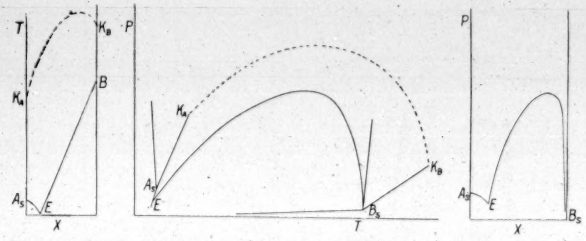
The critical liquid itself is, however, completely determined. At a temperature infinitely near to the critical solution temperature of the mixture, there are still three equations, and the critical solution is determined by the additional condition that the two phases become identical. We have, then, four equations; three of the type of 97, and the additional equation expressing the condition of identity between the two liquids, so this solution is uniquely determined.

If from the invariant point solid phenol-two liquids-vapor the water-rich layer disappears, we have the univariant equilibrium solid phenol-phenol-rich liquid and vapor. This will be the case if the total phenol content of the mixture be greater than that of the phenol-rich liquid. This is another branch of the solubility curve of phenol in water, or of the melting-point curve of phenol-water mixtures, and along it the solubility of phenol in water increases uniformly, until the melting point of phenol is reached. This curve does not differ in any important respect from the upper portion of the H_2O-KNO_3 curve, except that the melting point of phenol is so much lower than that of KNO_3 that probably the vapor pressure of the solutions decrease, without first rising to a maximum.

It will not be possible to illustrate any more types of equilibria in binary systems, but I believe that enough examples have been given to show the application of this type of treatment to heterogeneous equilibria. This is in my opinion the most natural and

simplest method of studying phase-rule problems, and if such problems were taken up in this manner in the text-books I believe chemists would have a clearer understanding of the fundamental problems underlying heterogeneous equilibria. As it is, there are only the two methods of approaching a problem; from the point of view of the empirical and, in most useful cases, wholly inaccurate dilute solution laws, or from the point of view of the usual statement of the phase rule as a qualitative guide in classification and outlining the problem, bolstered up by the theorem of Le Chatelier. The equation from which the phase rule was

FIG. 5.



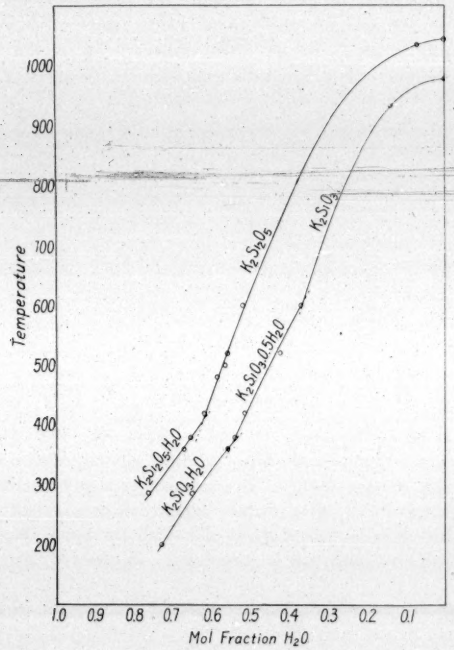
Diagrammatic temperature-concentration, pressure-temperature, and pressure-concentration projections for a binary system in which the fusion curve (EB_S) is not intersected by the critical curve ($K_A K_B$).

deduced is Gibbs' equation 97, and we have seen that the purely qualitative rule mentioned above is an incidental deduction from equation 97; the real meat of the equation is a quantitative guide to the changes in all the variables which define a system, and by the application of equation 97 in detail all the particulars in the behavior of a system can be predicted. Moreover, there is no restriction in the number of components to which this equation can be applied; general theorems in regard to the relations between phases may be deduced as readily for a system of n components as for a system of two components. I will give some examples of the deduction of purely general relations, and of the application of equation 97 to three-component systems, but before doing so there is an interesting point connected with the relations of systems such as water-salt at high temperatures that I desire to explain.

In a binary system composed of a non-volatile and a volatile component, for example, water and a salt, the solubility or fusion

curve is continuous from the eutectic to the melting point of the anhydrous component. This is shown diagrammatically in Fig. 5. At a temperature represented by the point K_A, component A shows the critical phenomena, and the critical temperature of B is at a higher temperature K_B. In this case the two curves are

FIG. 6.

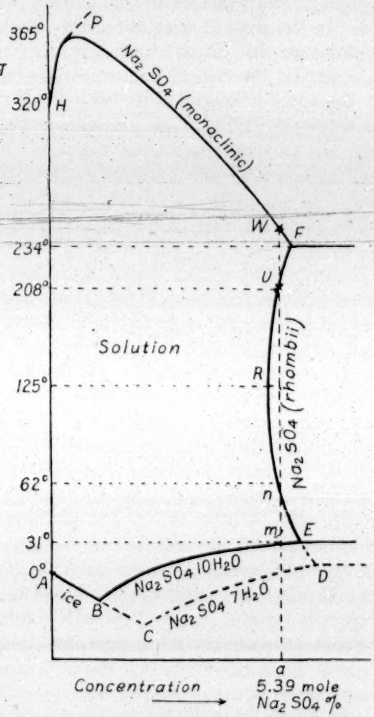


Solubility or fusion curves in the binary systems H_2O-K_2SiO_3 and H_2O-$K_2Si_2O_5$.

far apart over their entire course and no saturated solution shows the critical phenomena. This relation is shown, for example, by the systems H_2O-K_2SiO_3 and H_2O-$K_2Si_2O_5$, whose solubility relations are shown in Fig. 6. The melting points of these two compounds are both in the neighborhood of 1000°, far above the critical temperature of water, but that has no influence when the

solubility curve and the critical curve are far apart. Critical phenomena are not exhibited by the saturated solutions; it would be necessary to heat the solutions to a much higher temperature than any along the fusion curve in order to observe critical

FIG. 7.

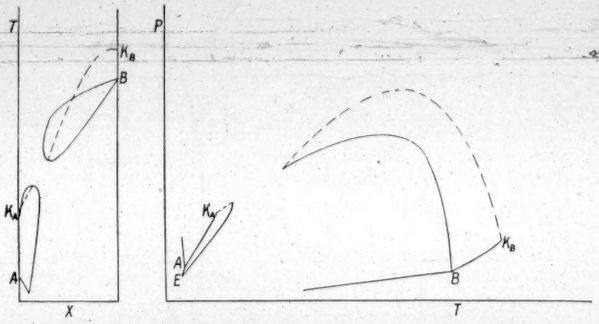


Solubility relations in the binary system H_2O-Na_2SO_4. The region of the first critical end-point has been exaggerated.

phenomena. Fig. 7 shows the variation in pressure along the saturation curve of the metasilicate and the disilicate, and it will be seen that the maximum pressure is far below the critical pressure of pure water.

In other systems, however, the critical phenomena are met with; if we consider the system water-sodium sulfate, for example, we know that the critical phenomena are shown at a temperature but slightly above the critical temperature of pure water. The low temperature portion of the solubility curve of Na_2SO_4 is shown in Fig. 7; the relations at the critical temperature are exaggerated. In the case of a solution, the critical temperature is always higher than that of the water, and it is generally, though not always, true that the critical temperature of each component is raised by the addition of the other component. In Fig. 8 the relations in a system of this type are shown diagrammatically.

FIG. 8.



Diagrammatic temperature-concentration and pressure-temperature projections for a binary system in which the fusion curve is intersected by the critical curve (K_AK_B).

A_a is the melting point of the volatile component, or, more properly speaking, the more volatile component; and K_a is its critical temperature. Now at the critical point, liquid and vapor have identical properties; if the liquid phase is a solution containing 5 per cent. dissolved material, the vapor phase also will contain 5 per cent. of the second component. As component B is added to A, the critical temperature of A is raised, but at first the critical phenomena are shown only by unsaturated solutions. As the content of B is increased, the fusion curve and the critical curve approach each other, until a point is reached at which the critical phenomena are shown by saturated solutions; at this point there are three phases, solid, liquid, and vapor, and in addition the vapor phase and the liquid phase are identical in properties. As

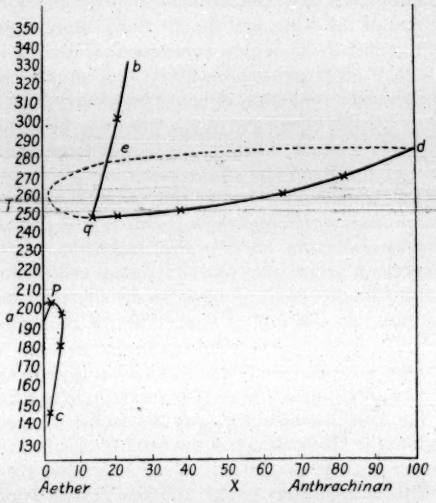
can be seen most readily from the pressure-temperature curve, at the critical temperature of the saturated solution the fusion curve is cut by the critical curve; this is called the first critical end-point in the system. It is evident that there must be two critical end-points. The melting point of the second component also is at a lower temperature than its critical temperature; since the critical curve is continuous from the critical temperature of one component to that of the other, and the solubility curve terminates at the melting point of the second component, if the fusion curve is cut in one point it must also be cut at a second point, at a higher temperature. At this second critical end-point also the compositions of the liquid and vapor must be the same; in the temperature-composition diagram the two curves showing the composition of the liquid and of the vapor merge into each other at the critical temperature, and at this point the resulting continuous curve has a horizontal slope. This is true of necessity at both the upper and at the lower critical end-points.

The solutions above the second critical end-point may be regarded from another point of view. In the simple system water-KNO_3, we saw that addition of water lowered the melting point of KNO_3, and also that for a certain composition range the vapor pressure of the saturated solutions increased with decreasing temperature; it required more and more pressure to keep the water on the job. The same is true in the cases in which critical end-points are formed, but in this case a point is reached at which the water can no longer be kept on the job, no matter what the pressure applied. This is analogous to the ordinary critical temperature; in the case of water, for example, as the temperature of the liquid is raised the pressure of the vapor increases, and it requires more and more pressure to keep the water liquid, until above the critical temperature it is no longer possible to liquefy the vapor by any amount of pressure. In the binary system, however, at the second critical end-point, as well as at the first, liquid and vapor have the same composition, so both components are contained in both phases. There is but one system that has been worked out of this type, the system ether-antraquinone, whose temperature-solubility relations are given in Fig. 9. The pressure-temperature relations are given in Fig. 10.

The application of equation 97 to three-component systems is merely an amplification of the methods previously applied to two-

component systems, except that in this case we have one more component, one more term of the form μdm in our original equation, one more term of the form $md\mu$ in equation 97, and one more term in our expression for the slope of the pressure-temperature curve. For a two-component system, the elimination

FIG. 9.



Temperature-concentration projection in the binary system ether-anthraquinone. The fusion curve cp-qd is intersected in the points p and q by the critical curve bq-p.

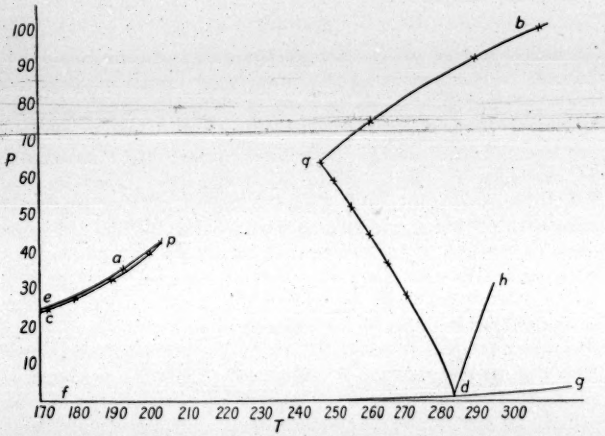
of the terms du_1, du_2 from the equations of the form of 97 for a univariant equilibrium gave the equation

$$\frac{dp}{dT} = \frac{s' - s'' + \frac{x' - x''}{x''' - x''}(s''' - s'')}{v' - v'' + \frac{x' - x''}{x''' - x''}(v''' - v'')}$$

in which the composition terms represent the difference in the content of the component to which x refers, say KNO_3 in the binary system water-KNO_3, in the various phases. When the phases with single, double and triple accents are vapor, liquid and solid, respectively, the coefficients are the composition differences

vapor-liquid and solid-liquid. When the compositions of the phases are plotted, as usual, along the base line of the graphical representation, the term $x^v - x^l$ represents the length of the line $x^v - x^l$; the term $x^s - x^l$, the length of the line $x^s - x^l$. In three-component systems it is customary to represent the composition by means of an equilateral triangle and the amounts of the three components are represented by x, y, and $(1-x-y)$. In this case the coefficients of the entropy and volume differences between the

FIG. 10.



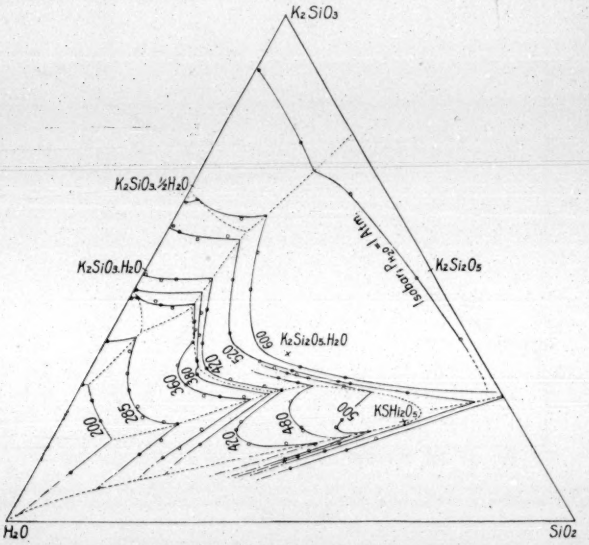
Pressure-temperature projection in the binary system ether-anthraquinone. The critical curve *eap-qb* intersects the P-T curve of the univariant equilibrium solid-liquid-vapor, *cp-qd*, in the points *p* and *q*.

phases, taken two by two, as before, no longer represent lengths, as in the two-component system, but areas of triangles whose apices represent the compositions of three phases. Since there are four phases, there are three entropy and volume differences, and the compositions can be represented by three areas. The equation in this case is

$$\frac{dp}{dT} = \frac{(s' - s'') + \frac{A_{124}}{A_{234}}(s''' - s'') - \frac{A_{123}}{A_{234}}(s'''' - s'')}{(v' - v'') + \frac{A_{124}}{A_{234}}(v''' - v'') - \frac{A_{123}}{A_{234}}(v'''' - v'')}.$$

The course of a P-T curve in a three-component system can be followed in the same manner with the aid of this equation that it was followed in a two-component system. There is no simple example to use in illustrating the application of this equation; as far as I know, but one system of three components, one of which is volatile, has been worked out, the system H_2O-K_2SiO_3-SiO_2,

FIG. 11.



Isothermal polybaric saturation curves in the ternary system H_2O-K_2SiO_3-SiO_2. An isobaric polythermal curve at 1 atm. pressure is also shown.

which is complicated by the formation of a number of compounds. However, the vapor phase is water only, and there is no solid solution formed, so the liquid phase is the only one of variable composition. The solubility or fusion relations in this system are shown in Fig. 11; the components are H_2O, K_2SiO_3 and SiO_2, and the solubility, or, better, the saturation relations at different temperatures are shown by means of curves. A detailed discussion of this system from the point of view we have just been

considering was published in the *Journal of the American Chemical Society* in January, 1918, and those interested will find there an example of the application of this method of attacking problems in heterogeneous equilibria to a complicated system, and also an illustration of the development of general laws to systems of any number of components. No one has yet worked out a four-component system in sufficient detail to afford an illustration of the theoretical treatment, but it is apparent that the extension of the methods exemplified for two and three components is not a difficult matter.

SUMMARY.

In this and the two preceding lectures we have seen that by means of the logical extension of the usual treatment of the two laws of thermodynamics to systems of several components a rigorous guide to the equilibrium relations between polyphase complexes in such systems is obtained. The method followed has been essentially that given by Gibbs in his "Equilibrium of Heterogeneous Substances," though only a small portion of that paper has been covered, merely that leading up to the derivation of equation 97. In the usual treatment of heterogeneous equilibrium the phase rule, an incidental qualitative deduction from equation 97, is used as a guide to the classification of complex equilibria, bolstered up by the theorem of Le Chatelier, a qualitative expression of the second law, in the further development with change in pressure and temperature. Equation 97 itself, however, affords not merely a qualitative, but a quantitative guide to the equilibrium relations in the most complex systems, and its detailed application serves to elucidate the most complicated relationships. The method of application of this equation has been exemplified in a series of examples, beginning with the simplest cases in one and two-component systems, then taking up in detail the more complicated cases of the formation of compounds in binary systems, both compounds with congruent and compounds with incongruent melting points, and further the formation of two liquid layers in a binary system. In addition the application to more complicated cases in both binary and ternary systems is indicated. The methods exemplified afford the most logical and natural treatment of phase-rule problems, and lead to the clearest understanding of the fundamental principles underlying heterogeneous equilibria.

LECTURE 4.

In the previous lectures I have dealt exclusively with univariant systems, systems in which there were enough phases to make possible the elimination of all the chemical potentials, giving equations which could be considered in terms of the convenient variables, pressure, temperature, and composition of the phases.

Now, an important group of laws in physical chemistry are those approximations known as the laws of dilute solutions. These laws express the fact that for sufficiently small additions of a solute, the properties of the solvent are proportional to the amount of solute present, and the usual expressions connecting the lowering of vapor pressure, lowering of the freezing point, and raising of the boiling point, are the quantitative expressions which result from the application of this fact to the processes in question.

While these laws are limited in their application to dilute solutions, there are special cases in which they give a fair approximation to the facts as determined by experiment over a considerable range of composition. Partly because of this fact, attempts have been made to extend these laws to concentrated solutions, and to explain the real deviations from these laws by assumptions as to the molecular complexity of solvent, solute, or both; assumptions which in themselves oftentimes are plausible. It should be borne in mind, however, that before we consider deviations from these laws, developed for dilute solutions, as proof that such assumptions, plausible though they may be, are in accord with facts, we should carefully examine the assumptions upon which the laws themselves are based. For this purpose a method of derivation which first develops general relations without assumptions as to the molecular condition of the components—often the point at issue—and then deduces the dilute solution approximations by means of explicit assumptions, is desirable. Such a method of treatment is indicated by Gibbs, and this lecture is an amplification of the methods used by him.

It will be observed that in all these cases we have, not three but two phases in a two-component system, and consequently the system is divariant. We have two equations of the type of 97, and hence can eliminate but one of the two chemical potentials. The laws of dilute solutions aim to provide another relation

between the variables, such that the system becomes univariant; to do this it is necessary to evaluate the changes in chemical potential. The chemical potential of any component depends on the pressure, the temperature, and the composition; in a two-component system the chemical potential of the solute can be changed only by changing the pressure, the temperature, or the concentration of the solute. The total change in chemical potential is the integrated sum of the rate of change of chemical potential with change in pressure, multiplied by the amount the pressure changes; plus the rate of change with temperature, multiplied by the change in temperature; plus the rate of change of chemical potential with change in the concentration, multiplied by the change in concentration. In the form of an equation, this becomes

$$d\mu = \left(\frac{\partial \mu}{\partial p}\right) dp + \left(\frac{\partial \mu}{\partial t}\right) dt + \left(\frac{\partial \mu}{\partial x}\right) dx,$$

and our problem is to evaluate the rate of change of chemical potential with pressure, temperature, and composition, the quantities, $\left(\frac{\partial \mu}{\partial p}\right), \left(\frac{\partial \mu}{\partial T}\right), \left(\frac{\partial \mu}{\partial x}\right)$.

To do this we will go back to our original equations.

We have seen before that when a quantity of heat, dQ, is added to an isolated system at constant pressure, p, the energy is increased and work is done against the pressure, and the relation between the heat added, the work done, and the increase in intrinsic energy is given by the equation

$$dQ = d\epsilon + pdV.$$

For dQ, the quantity of energy added as heat, we may substitute the product of the intensity factor of heat energy, temperature, into the change in the quantity factor, entropy, and the equation becomes

$$d\epsilon = TdS - pdV.$$

This means that the total change in energy is the sum of the energy added as heat and the energy expended as work, and the intrinsic energy is expressed as a function of the entropy and volume. In case the system contains several independently variable components, the energy can be changed by changing the

amount of any one of these components; the energy in this case is not only a function of the entropy and volume, but also of the mass of each component, and the equation accordingly becomes

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

in which m_1, m_2, . . . m_n refer to the masses of the different components, μ_1, μ_2, . . . μ_n to a quantity called the chemical potential and defined as being the increase in energy of the system resulting from the addition, dm, of the component in question, at constant entropy, volume, and quantities of the other components. This equation may be considered as representing the energy of an infinitesimal portion of the total mass as the summation of the heat, volume, and chemical energies. It may be integrated by adding up all such similar portions of the mass, by which integration we obtain the equation

$$\epsilon = TS - pV + \mu_1 m_1 + \mu_2 m_2 + \ldots\ldots + \mu_n m_n.$$

If this integrated equation be again differentiated, regarding both the intensity and quantity factors as variable, and the result compared with the original equation, we get equation 97,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n.$$

There are some other thermodynamic quantities in common use which I will now define, and at the same time point out the difference in notation and nomenclature between various writers. Incidentally, the intrinsic energy, which I have denoted by the Greek letter ϵ, is oftentimes denoted by U. If to the intrinsic energy ϵ be added the work energy pV, we get a quantity which is called the "heat content" of the system at constant pressure; this quantity was called by Gibbs the chi function, and is now commonly denoted by H:

$$H = \epsilon + pV$$
$$dH = -TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2.$$

That this represents the heat content at constant pressure is evident from the following considerations. If we consider a system changing from one condition to another as a result of the addition of heat, and indicate the original condition by unprimed letters, the final condition by single primes, we will get for the difference in the value of H in the two states the relation

$$H' - H = (\epsilon' - \epsilon) + p(V' - V)$$

since the pressure is constant. But if we turn to the equation

$$dQ = d\epsilon + pdV$$

we see that the change in the quantity H is numerically equal to the heat added, and is greater in the final state, after the addition of heat, than in the original state. If a reaction takes place in a calorimeter at constant pressure, the heat given out is dQ, and the value of H in the final state is less than in the original state; if dQ, positive, represents heat given out, ΔH, the change in the heat content, is negative.

Similarly, if we consider as one function the combined values of the intrinsic energy and the heat energy, we get a quantity which represents the work capacity of the system; this was called by Gibbs the psi function, and by Helmholtz the free energy, and is the quantity usually meant by the term free energy. I will call it the psi function, because of the confusion of nomenclature, as that at least cannot be confused. We have then,

$$\psi = \epsilon - TS.$$
$$d\psi = -SdT - pdV + \mu_1 dm_1 + \ldots\ldots + \mu_n dm_n.$$

That this represents the work is also evident from our original equation. If we consider that the system changes from one state to another, at constant pressure, the work done is the pressure times the change in volume:

$$p(V' - V);$$

and if we consider the difference in the psi function in the original and final state, we get

$$\psi' - \psi = (\epsilon' - \epsilon) - T(S' - S).$$

Comparing this with the original equation

$$d\epsilon = TdS - pdV, \text{ or } d\epsilon - TdS = -pdV$$

we see that the change in the quantity psi is equal to the work done by the system against pressure; when the original volume is smaller than the final volume the system has done work at the expense of its psi function or free energy, which is accordingly less, as is indicated by the negative sign.

A third thermodynamic quantity in common use is that obtained by combining the intrinsic heat and work energies into one, called by Gibbs the zeta function:

$$\zeta = \epsilon - TS + pV.$$

This is a quantity of the greatest importance; it is the quantity called by Lewis the free energy, with the difference that Lewis's

free energy refers to a mol of the substance, while the zeta function as defined by Gibbs refers to a mass of $m_1 + m_2 + m_n$ grams.

If we differentiate the zeta function, considering both intensity and quantity factors as variable, we get

$$d\zeta = d\epsilon - TdS + pdV - SdT + Vdp.$$

But from the equation

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

we see that

$$d\epsilon - TdS + pdV = \mu_1 dm_1 + \mu_2 dm_2 + \mu_n dm_n,$$

so we get

$$d\zeta = Vdp - SdT + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n.$$

From this equation we can find two of the three quantities needed to fix the changes in the chemical potential of a substance, namely, the rate of change in chemical potential with pressure, $\partial\mu/\partial p$, and the rate of change of chemical potential with temperature, $\partial\mu/\partial T$. At constant temperature and constant quantities of the other components, *i.e.*, if dT, dm_2, ... dm_n are zero, we get

$$d\zeta = Vdp + \mu_1 dm_1$$

and further

$$\left(\frac{\partial\zeta}{\partial p}\right)_{Tm} = V \text{ and } \left(\frac{\partial\zeta}{\partial m}\right)_{Tpm} = \mu_1$$

in which the subscripts indicate the quantities to be taken as constant, the symbol m without subscript indicating all the masses except the one, if any, with respect to which we are differentiating. Now if we differentiate each of these again, the first with respect to m_1, the second with respect to p, we will get

$$\frac{\partial^2\zeta}{\partial p\partial m_1} = \frac{\partial V}{\partial m} \text{ and } \frac{\partial^2\zeta}{\partial m_1\partial p} = \frac{\partial\mu_1}{\partial p}.$$

Since the order in which we differentiate is immaterial, these two quantities must be equivalent to each other:

$$\frac{\partial\mu_1}{\partial p} = \frac{\partial V}{\partial m_1}.$$

We thus have arrived at an expression for the rate of change in chemical potential with change in pressure, and find it to be equal to the rate of change of total volume with the quantity of the component, at constant temperature and mass of the other components. If we plot the volume of a solution containing 100

grams of water against the number of grams of salt, we get a curve whose slope at any point, $\frac{\partial V}{\partial m_2}$, is equal to the rate of change of chemical potential of the salt at that temperature and composition. This quantity $\frac{\partial V}{\partial m_2}$ is called by several different names. Lewis calls it the partial volume of the salt, and a more usual name is the differential volume; probably both are suggested by the fact that $\frac{\partial V}{\partial m_1}$ is a partial differential. Other writers call it the "fictive" volume, which is rather a misnomer. I prefer to call this, and other similar quantities, by the name "effective," as suggested by Doctor Williamson of our laboratory. The effective volume is exactly what the quantity really is; it is the value of the volume which is effective in considering the chemical and thermodynamic properties of the solution. Following the notation of Lewis, the quantity $\frac{\partial V}{\partial m_1}$ is often written $\bar{v}_1$; lower case, to indicate that it is a specific quantity, and with a bar over it.

The rate of change of the chemical potential with temperature may be obtained in a similar manner. If we consider the zeta function at constant pressure, we get

$$d\zeta = -SdT + \mu_1 dm_1,$$

and by again differentiating the derivative of this as before, but with respect to temperature and quantity of component m_1, we get

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{pm} = -\left(\frac{\partial S}{\partial m_1}\right)_{pm} = -\bar{s}_1.$$

The rate of change of chemical potential with respect to temperature is equal to, but opposite in sign to, the rate of change of entropy with mass of the component, that is, to the "effective" entropy of m_1 in the solution. As is always the case, the entropy concept is more difficult to explain than the volume concept, though both are quantity factors of energy, but in the case of a saturated solution, the effective entropy is the differential heat of solution, the heat absorbed when one gram of the salt dissolves in a very large quantity of the almost saturated solution, divided by the absolute temperature.

We thus have evaluated two of the three rates of change of chemical potential; incidentally, we may get from this same equa-

tion, and from the original equation as well, a useful relation between the changes of chemical potential of the various components. At constant pressure and temperature, the differential of zeta is

$$d\zeta = \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n,$$

and by proceeding as before we get

$$\frac{\partial \mu_1}{\partial m_2} = \frac{\partial \mu_2}{\partial m_1}.$$

But this does not give us a relation between chemical potential and concentration, and indeed such a general relation cannot be obtained on thermodynamic considerations alone. Under certain conditions the form of a possible relation is indicated by thermodynamic reasoning, and by the introduction of a number of assumptions, extraneous to thermodynamics, such a relation can be obtained.

If we apply equation 97 to a system of two components, at constant pressure and temperature, we get

$$m_1 d\mu_1 + m_2 d\mu_2 = 0.$$

If we take a constant quantity of m_1, for example water, and add a small amount of salt, dm_2, the change in the chemical potentials of water and salt is given by

$$m_1\left(\frac{\partial \mu_1}{\partial m_2}\right) + m_2\left(\frac{\partial \mu_2}{\partial m_2}\right) = 0.$$

As the solution considered is more and more dilute, m_2 approaches zero, and if we are considering the addition of the quantity of salt dm_2 to pure water, m_2 is zero. But if m_2 is zero, and the sum of the terms

$$m_1 \frac{\partial \mu_1}{\partial m_2} \text{ and } m_2 \frac{\partial \mu_2}{\partial m_2}$$

is to equal zero, either

$$\frac{\partial \mu_1}{\partial m_2} = 0,$$

in which case we get

$$m_1 \text{ times zero} + \text{zero times} \frac{\partial \mu_2}{\partial m_2} = \text{zero},$$

and $\frac{\partial \mu_2}{\partial m_2}$ may be a finite quantity, or, if $\frac{\partial \mu_2}{\partial m_2}$ is not zero, the first term, $m_1 \frac{\partial \mu_1}{\partial m_2}$, is not zero, and $\frac{\partial \mu_2}{\partial m_2}$ must be infinity; for only infinity multiplied by zero can equal a finite quantity.

Of these alternatives, the only possible one is that $\partial \mu_2 / \partial m_2$ is infinity, in which case $\partial \mu_1 / \partial m_2$ must be a finite negative quantity. It is evident that this is in accord with facts. If we have water in contact with vapor, and add salt to the water, some vapor will be condensed as the vapor pressure of the solution is lowered; the potential of water in the solution has decreased as a result of the addition of salt. As the amount of salt added be decreased to an infinitesimal amount, it is not probable that the effect of its addition would approach zero, as would be the case if $\frac{\partial \mu_1}{\partial m_2} = 0$, but it is much more probable that its effect would approach a small constant negative value, as is required if $\frac{\partial \mu_2}{\partial m_2} = \infty$. We may then consider that as the solution becomes more and more dilute, that is, as m_2 approaches zero, the value of $\frac{\partial \mu_1}{\partial m_2}$ should approach a finite negative quantity. If we replace this expression by the expression $-A/m_1$, the value of A will be positive and independent of m_1. Substituting $-A/m_1$ for $\frac{\partial \mu_1}{\partial m_2}$ we get

$$m_1 \left(- \frac{A}{m_1} \right) + m_2 \frac{\partial \mu_2}{\partial m_2} = 0$$

or

$$\frac{\partial \mu_2}{\partial m_2} = \frac{A}{m_2}.$$

The above has been straightforward reasoning with no assumptions, and we are therefore justified in stating that in dilute solutions the potential of the salt tends to approach a constant value of this form. Unfortunately, however, this is not of much aid; it marks the limit to which we may go on the basis of the first and second laws of thermodynamics alone.

In another place Gibbs carries the problem a step further. It can be shown that in an ideal gas—this is the first time that this much-abused term has been brought in—in an ideal gas the chemical potential μ is given by the expression

$$\mu_2 = B + AT \, ln \frac{m_2 v}{V v}$$

in which B is a constant and A is the gas constant for 1 gram;

that is, R/M, in which M is the molecular weight. It is to be emphasized that A is not a universal constant, as is R. Now if we have a liquid phase in equilibrium with the gas, and if the law of Henry applies, the ratio of the concentration of the substance in the two phases is constant:

$$\frac{m_2^l}{V^l} = K \frac{m_2^v}{V^v}.$$

We may therefore replace the ratio $\frac{m_2^v}{V^v}$ of the equation for μ by $\frac{m_2^l}{KV^l}$. Making this substitution,

$$\mu_2 = B + AT \ln \frac{m_2^l}{KV^l}.$$

The term V^l represents the total volume of the liquid phase considered, composed of $m_1 + m_2$ grams of the two components. If we represent the specific volume of this phase by lower case v, evidently

$$V^l = (m_1 + m_2)\, v,$$

and the equation becomes

$$\mu_2 = B + AT \ln \frac{m_2^l}{K (m_1 + m_2)\, v}.$$

If now we differentiate this equation with respect to m_2, regarding v and m_1 as constant, we get

$$\frac{\partial \mu_2}{\partial m_2} = AT \frac{m_1}{m_1 + m_2} \cdot \frac{1}{m_2}.$$

If we call $x = \frac{m_2}{m_1 + m_2}$ at constant m_1,

$$\partial x = \frac{m_1}{(m_1 + m_2)^2} \partial m_2;\ \partial m_2 = \frac{(m_1 + m_2)^2}{m_1} \partial x.$$

Substituting this value of dm_2 we get

$$\frac{\partial \mu_2}{\partial x} = AT \frac{m_1 + m_2}{m_2} = \frac{AT}{x}.$$

This gives us a value for the quantity sought, the change in chemical potential with composition, but this value is no longer free from assumption. In deriving it we assumed (1) that the vapor phase obeyed the ideal gas laws, (2) that the law of Henry applied to the distribution of m_2 between the vapor and liquid phases, and (3) that the specific volume was independent of the

amount of m_2 present. But the value of A still refers to the gas constant for one gram of the vapor; van't Hoff was the first to replace this by the universal gas constant, R. To do this, we have only to remember that the molecular weight, M times the constant for one gram, gives the constant for one mol, *i.e.*, $A = R/M$. Making this substitution, we find that

$$\frac{\partial \mu_2}{\partial x} = \frac{RT}{M_2 x}.$$

Similarly, for component, m_1,

$$\frac{\partial \mu_1}{\partial x} = \frac{RT}{M_1 (1 - x)}$$

in which M_1 and M_2 are the molecular weights of the substance in the vapor. It is easy from this point to deduce the laws of dilute solutions.

Let us first consider the equilibrium between a solution of a non-volatile salt in water and derive the change in vapor pressure with composition. It is a fundamental condition of equilibrium that the chemical potential of the water must be the same in the two phases. Now the potential of water in the vapor at constant temperature depends only on the pressure of the vapor, while the potential of the water in the solution depends on the pressure and composition; since the potential of water in the two phases must remain the same, these two changes must be equal. The change in potential of water in the vapor is given by the rate of change of potential with pressure multiplied by the change in pressure, $d\mu_1^v = \left(\frac{\partial \mu_1}{\partial p}\right)^v dp$. Similarly, the change in potential in the liquid is

$$d\mu_1^l = \left(\frac{\partial \mu_1}{\partial p}\right)^l dp + \left(\frac{\partial \mu_1}{\partial x}\right)^l dx,$$

Since the two changes must be equal for the phases to remain in equilibrium

$$\left(\frac{\partial \mu_1}{\partial p}\right)^v dp = \left(\frac{\partial \mu_1}{\partial p}\right)^l dp + \left(\frac{\partial \mu_1}{\partial x}\right)^l dx.$$

But we have previously seen that

$$\frac{\partial \mu_1}{\partial p} = \frac{\partial V}{\partial m_1} = \bar{v}_1; \quad \frac{d\mu_1}{\partial x} = \frac{RT}{M_1 (1 - x)};$$

substituting,

$$\left(\bar{v}_1^{\,v} - \bar{v}_1^{\,l}\right) dp = \frac{RT}{M_1 (1 - x)} dx.$$

Since the solution is dilute, $\bar{v}_1{}^l$ for the liquid is essentially the specific volume of the liquid, and, since the vapor is pure H_2O, $\left(\frac{\partial V}{\partial m_1}\right)^v$ is the specific volume of the vapor. The specific volume of the liquid is negligible; since we have already assumed the gas laws, we may write for the specific volume of the vapor,

$$v = \frac{RT}{M_1 p}.$$

Substituting

$$\frac{RT}{M_1}\frac{dp}{p} = \frac{RT}{M_1}\frac{dx}{1-x}$$

$$d\,ln\,p = -\,d\,ln\,(1-x).$$

This may be integrated, remembering that when $x = 0$, the liquid is pure water whose vapor pressure is p_0. We thus get

$$ln\frac{p}{p_0} = ln\,(1-x)$$

$$\frac{p}{p_0} = (1-x)$$

$$\frac{p_0 - p}{p_0} = x.$$

The relative lowering of the vapor pressure is equal to the percentage of salt in the solution, which is one statement of Raoult's law.

The other dilute solution approximations are as simply obtained. If we consider the lowering of the freezing point of water by a dissolved salt, we again have two phases, one of which is pure ice, the potential of which is a function of the temperature; the other a solution, the potential of water in which is a function of the temperature and the concentration. Equating the change in μ as before,

$$\left(\frac{\partial \mu}{\partial T}\right)^s dT = \left(\frac{\partial \mu}{\partial T}\right)^l dT + \left(\frac{\partial \mu}{\partial x}\right)^l dx$$

$$\frac{\partial \mu}{\partial T} = -\frac{\partial s}{\partial m_1} = -\bar{s}_1$$

$$(\bar{s}_1{}^l - \bar{s}^s)\,dT = \frac{RT}{M_1(1-x)},$$

in which $\bar{s}_1{}^l$ is the effective entropy of water in the solution, $\bar{s}_1{}^s$, the specific entropy of ice.

If we put the effective entropy of water in the solution as equal to the specific entropy of water at the same temperature, this becomes

$$\left(s^{l} - s^{s}\right) dT = \frac{RT}{M_1 (1 - x)} dx.$$

But $(s^l - s^s) = \frac{L}{T}$, where L is the latent heat of fusion. Hence

$$L \frac{dT}{T} = \frac{RT}{M_1} \frac{dx}{1 - x}, \text{ or}$$

$$\frac{dT}{T^2} = \frac{R}{M_1 L} \frac{dx}{1 - x}.$$

Integrating, remembering that when $x = 0$, $T = T_0$, we get

$$\left(\frac{1}{T} - \frac{1}{T_0}\right) = \frac{R}{M_1 L} ln\,(1 - x)$$

or

$$T_0 - T = \frac{RTT_0}{M_1 L} ln\,(1 - x).$$

If x is very small, x is approximately equal to $ln(1-x)$, and T differs but little from T_0. The equation then becomes

$$\Delta T = T_0 - T = \frac{RT^2}{M_1 L} x.$$

This is the usual form for the freezing point lowering of dilute solutions. The further relations, such as the raising of the boiling point by a dissolved solute, are obtained in a similar manner.

It is evident, then, that by making certain assumptions we are able to arrive at the usual form of the dilute solution approximations; and it is also evident that as soon as we make these assumptions, the equations lose their unexceptionable character and become no more certain than the assumptions introduced. Of these, those relating to the application of the gas laws to the vapor and to the neglect of the volume of the liquid in comparison to that of the vapor, do not introduce very large errors, and the magnitude of these errors can be calculated. It will be observed that there is no assumption involved in the derivation of the first form of the approximation equation, $d\mu_2/dm_2 = A/m_2$, except that this expression is derived explicitly for the case that the quantity of the component m_2 is very small; this equation merely states that for small amounts of salt m_2, the change in the chemical

potential of the water approaches a constant value, $-A/m_1$, that of the salt, A/m_2. But to identify this constant A with the universal gas constant, it is necessary to introduce some assumption, such as Henry's law. After making this assumption, Raoult's law and the usual expressions for the lowering of freezing point and raising of the boiling point follow immediately; but after all, there is very little difference between assuming Henry's law and Raoult's law. The relation expressed in the equation $\frac{\partial \mu_2}{\partial x} = \frac{RT}{M_1 x}$, or at least in the equation, $\frac{\partial \mu_2}{\partial m_2} = \frac{A}{m_2}$, undoubtedly expresses a fundamental law for dilute solutions. When we come to apply these relations to solutions which are not dilute, we get into such difficulties as are involved in trying to apply Raoult's law to a system forming two liquid layers; the vapor pressure of water is the same from the water-rich and from the water-poor layer, although these may contain as widely differing percentages of water as 99 and 1. Deviations from Raoult's and associated laws are oftentimes taken as evidence of molecular complexity of the solvent or solute, or a combination between the two, and I have no doubt that all these processes do take place. But before accepting these deviations as proof that there are such molecular rearrangements, and especially before these deviations are taken as a measure of the extent to which the process has taken place, we should bear in mind that agreement with these laws represents a particular combination of special conditions; the surprising thing is, not that the dilute solution laws are not applicable over a greater range of composition and to a greater variety of substances, but that they do give a fair approximation to the facts in so many cases. In considering a general theory of dilute solutions, we should not expect that such a theory should provide us with an exact and generally applicable expression for $d\mu/dx$, that is, that we should be able to calculate all the properties of all chemical combinations without experiment. The problem is far too complicated for that; we are unable to state the basic relationships which occasion such differences in behavior as the formation of a salt hydrate in one case and the failure of such a hydrate to form in another; or the basic relationships which occasion such differences in behavior as are shown by systems forming two

liquid layers. To me, it appears best to interpret our experimental results in the light of the certain fundamental laws of thermodynamics, and by further study of systems from this point of view, possibly to arrive at some general relation which will give us a deeper insight into the mechanism of chemical action.

SUMMARY.

The underlying purpose of these lectures has been to present, in as simple a form as possible, the fundamental features of that portion of Gibbs' great paper, "Equilibrium of Heterogeneous Substances," which lead up to, and are essential to, the development of equation 97. As has been emphasized throughout, this equation is a powerful weapon for attacking the problem of equilibria between phases, and affords a more direct and simple, as well as a far more potent, attack than does the usual statement of the phase rule, which is but an incidental qualitative deduction from equation 97. By the detailed application of this equation problems of heretogeneous equilibria may be solved completely if the entropy and volume changes are known in their entirety. But more than this, by the application of this equation, and such a general knowledge of entropy and volume differences as are involved in the knowledge that a vapor phase has a greater entropy and volume than the liquid phase with which it is in equilibrium, or that the high-temperature modification of a phase has a greater entropy than the low-temperature modification, it is possible to predict, with an approach to quantitative accuracy, the behavior of the system when subjected to changes in pressure, temperature, and composition. Furthermore, this thermodynamic method is not limited in its application to two or three-component systems, but can be extended readily to include any desired number of components.

A sharp line must be drawn between those relations which are derived from the two laws of thermodynamics without the aid of further assumptions, and those whose derivation involves not only the thermodynamic laws proper, but also further assumptions extraneous to thermodynamics. To this latter clan belong the dilute solution approximations. In dealing with dilute solutions it is usual to assume some relation between composition and thermodynamic properties which will enable a divariant equi-

librium such as that between ice and a dilute salt solution to be treated as a univariant equilibrium. It was shown by Gibbs that when the amount of one component approaches zero, such a relation becomes possible, and he indicated the form the relation would take. Making certain explicit assumptions, he further identified the constant value which the rate of change of the potential of water with addition of salt approaches as the amount of salt approaches zero, with the gas constant for one gram of the solute. Making these assumptions, the derivation of the ordinary dilute solution laws is easy, and this method of derivation has the advantage of confronting us squarely with the assumptions involved in these dilute solution approximations.

The Dezincification of Brass.—It has long been known that the standard brass consisting of copper and zinc will lose its zinc at a greater ratio than the copper under a variety of circumstances; even when constantly in contact with a fairly pure water, the zinc may be so completely removed as to leave nothing but a brittle porous mass of copper. Mr. Ralph B. Abrams of the senior class in Chemical Engineering, University of Wisconsin, presented a paper at the forty-second general meeting of the American Electrochemical Society in September, describing a research to determine the manner in which this removal of zinc takes place under ordinary conditions. His conclusion is as follows:

The first step is the dissolving of the brass as a whole. The copper in solution then redeposits replacing brass as a unit. This redeposition will not take place unless there is some means of holding the dissolved copper in contact with the brass. This can be accomplished in two ways, one by the presence of a membrane, the other by having a large excess of dissolved copper present. Obviously this latter possibility is a remote one, especially so far as natural conditions are concerned. The membrane may be anything whatsoever, so long as it performs the function of keeping the dissolved copper in contact with the brass. Cuprous chloride is the usual membrane. Whether or not dezincification shall take place can be controlled by merely supplying or taking away the membrane. Briefly then, the dezincification of brass is the dissolving of the brass as a whole, the holding of the dissolved copper in contact with the brass by a membrane, and the subsequent redeposition of the copper.

H. L.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.

I.
THE DISTRIBUTION OF SENSITIVITY AND SIZE OF GRAIN IN PHOTOGRAPHIC EMULSIONS.*

BY

E. P. WIGHTMAN, A. P. H. TRIVELLI AND S. E. SHEPPARD.

THE problem of the "latent photographic image" has not infrequently excited curiosity and interest outside purely photographic circles. It has been an "imponderable," in some ways less susceptible of exact measurement than atom or electron. Arguments in favor of a chemical or physical nature have held the field without the deadlock being broken. To the problem of the "latent image" there has been added that of "sensitivity." On the one hand, it has been recently suggested that, at least in one and the same emulsion, this is nothing but an affair of geometry and probability.[1] Sensitivity, on this view, is only the *chance* of a grain, or connected group of grains, being hit by a light-quantum, hence, for unshadowed grains, is strictly a matter of projective area. On the other hand, chemists and emulsion-makers have arrived at a substantial theory of sensitiveness which in its most recent developments [2] tends to identify the substances of "sensitiveness" with both the latent and the developed image, as dispersed or colloid silver. As noted in more detail later, it may be assumed that in the silver bromide grain of emulsions there exists, owing to reducing conditions in preparing the emulsion, a specific, or even individual, distribution of a photocatalyst.

* Communicated by Dr. C. E. K. Mees, Director; Communication No. 142 from the Research Laboratory of the Eastman Kodak Company.

[1] Cf. L. Silberstein: "A Quantum Theory of Photographic Exposure." Paper read before Am. Asso. Adv. Sci. (Toronto, 1921) *Phil. Mag.*, **44**, 257 (1922).

[2] Lüppo-Cramer: "Kolloid-chemie u. Photographie," 2d Ed.; F. F. Renwick: *J. Soc. Chem. Ind.*, 1920, p. 156T; A. P. H. Trivelli and S. E. Sheppard: "Monograph on the Silver Bromide Grain of Photographic Emulsions," Research Laboratory of the Eastman Kodak Company; S. E. Sheppard: *Phot. J.*, 1922, p. 88.

This is very feasibly a nucleation of colloid silver amicrons, dispersed in the silver halide lattice. Differential sensitivity of grains, on this view, depends upon this distribution of sensitizing nuclei; any probability function found valid either for variation of sensitivity amongst grains of the *same size*, or relating sensitivity to size of grain, enters in the process of emulsion preparation, rather than in that of exposure.

We propose, in this and subsequent papers, to examine these hypotheses, to note wherein they lead to similar conclusions, and as far as possible to test experimentally between them. The hypothesis of a discrete structure of light is of great theoretical significance; practically, the problem posed is of fundamental importance in the photographic industry.

In this paper is presented (1) a statement of the problem, with a discussion of some previous work on the photochemical law for the silver halide grain; (2) a correlation theory of the size-frequency of photographic emulsions and their sensitometric characteristics; (3) a comparison of theories of the relation of sensitivities and size distribution to the density exposure function. The material of part (2) will be dealt with more fully in another place and connection.[3] Its presentation is necessary in order that the very varied "disperse" character of photographic emulsions may be realized, as also the broad statistical basis of the connection of grain size with emulsion speed.

I. STATEMENT OF THE PROBLEM.

It has already been pointed out that in earlier work (H. and D., etc.) consideration of individual variations of the grains of silver halide emulsions was lacking. It is now known that the elementary grains are definite crystals of one system and class, but that in a given emulsion they vary:

1. In total size or volume;
2. In cross-section or projective area;
3. In shape.

It may be further considered possible, even probable, that wide variations of "sensitivity" exist among the grains of one and the same emulsion. We may initially define "sensitivity" as the

[3] Cf. *J. Phy. Chem.*, in press.

reciprocal of the energy required to make a grain developable by a developer of given reduction potential. It is generally accepted at present that the condition for developability is a nucleus, *i.e.*, that the photo-effect, whatever its nature, is localized in the grain. The most concrete development of this is that the nuclei consist of colloid silver, either provided (in part at least) by photolysis of silver halide, or formed by condensation of pre-existent colloid silver amicrons to submicrons. This latter hypothesis is due to F. F. Renwick. His primary contention, that the sensitive substance is not silver halide at all, but colloid (metallic) silver has recently received support from some remarkable experiments of F. Weigert.[4] In any case, if we attribute a definite sensitivity to a grain, this means that a certain finite increment of energy is necessary for developability. In the general problem of chemical reactivity, what has been termed the *critical energy increment*[5] of a molecule is analogous to this "inertia" of the grain, the reciprocal of its sensitivity.

Considering the variable of sensitometry, the density D, it must be remembered that to a near approximation grains contribute, on complete development, to density in proportion to their number and size conjointly, or again, to a slightly lower approximation, to their number and projective area. The quotient

$$\frac{\Delta D}{\Delta E} = \frac{\text{density increment}}{\text{energy increment}}$$

reckoned per unit area, would appear *a priori* to be independent of the size of grain, assuming a continuous wave-front. But if conditions permit a local concentration of energy related to the size of grain, the magnitude of the above quotient will depend upon the distribution of grain sizes in unit area.

Supposing a continuous wave-front, that is, *not* a quantum-like or discrete structure of radiation, local condensation of the energy to the critical increment might be effected in the material: (1) By reason of a variable distribution of a photochemical catalyst in the material, or specifically, among the grains. The probability of a grain reaching the critical increment would then depend upon its having a certain amount, and perhaps individual distribution, of the catalyst, the primary function of which would

[4] *Sitz. ber preuss. Akad. Wiss.*, 1921, p. 641.

[5] W. McLewis: "System of Physical Chemistry," vol. iii, p. 140.

be to increase the energy density of absorbable type.[6] Colloid silver submicrons supply a concrete example. Alternatively, it may be supposed that the silver halide is itself relatively inert, and with Renwick that the colloid silver particles are the true photosensitive material. In either case, the distribution of the "catalyst" could depend on the size of the grains, *e.g.*, the probability of a grain having sufficient catalyst might be proportional to its mass. *In this case, the sensitiveness-variation curve would coincide, to a first approximation, with the size-frequency curve,* for one and the same emulsion. (2) Local condensation and a sensitivity variation might be effected, as suggested in Toy's paper,[7] by optical conditions of refraction, reflection, etc., within the grain but depending on chance orientations and concentrations of the crystalline grains. Such a hypothesis is difficult to prove or disprove, but the statistical data being accumulated may strengthen or weaken its plausibility.

There remains, by exhaustion, the possibility of local, or granular, concentration of energy not by virtue of inherent factors of the sensitive material, not by accidental circumstances in its disposition, but as a necessary consequence of a discrete structure of the energy itself.[8]

The mathematical development of this assumption has been dealt with by Dr. L. Silberstein. It may, however, be pointed out here that to a large extent it gives the same relation between effective sensitivity variation and size-frequency distribution as that previously discussed on the hypothesis of a photocatalyst distributed amongst grains with a probability varying as their masses. On the quantum theory, however, it is the projective area which is fundamental rather than the mass. The important modifying factor of "clumping," or secondary aggregation of the primary grains, will be noted in connection with the results of measurements of size-frequency.

We advance later an approximate theory of the photochemical law for the single silver halide grain. Hence it appears desirable to examine more closely the experimental results of R. Slade

[6] Cf. W. McLewis: "System of Physical Chemistry," vol. iii, p. 140 (1919).

[7] *P. J.*, **61**, 417 (1921). We may note here, in connection with the data given later, that in *thick* grains the *position* of a photocatalytic centre might vary in grains of same size and shape.

[8] Cf. F. E. Ross: *Astrophys. J.*, **52**, 96 (1920).

and G. I. Higson,[9] since they propose as a result of these an empirical formula expressing "the photochemical law of the silver halide grain." Further, Higson has used these results, and this formula as a basis for deduction of density-exposure functions and ideal characteristic curves.[10] Essentially, their data consist in counts of numbers of grains in a one-grain layer made developable by increasing exposure, impressed either by increasing intensity for constant time, or by increasing time for constant intensity. They considered that in the emulsion used all the grains were of the same size, which appears doubtful to us, in view of our results with similar emulsions. But, passing this by, they advance a further postulate.[11] "All experimental evidence leads to the conclusion that all grains in one emulsion behave identically if they are of the same size." This is contrary to results of Svedberg[12] and has since been directly rebutted by Toy,[13] yet it is quite fundamental to their argument and mode of presenting their data.

They state,[14] "If (following Einstein) it is assumed that light is discrete in its nature, and that it is only necessary for one of these light quanta to be absorbed by a grain to make it developable, then if there were a number of grains, a, present on the plate, and they were exposed to a light of intensity, I, for a time, t, after which time x grains had been made developable,

$$\frac{dx}{dt} = kI(a - x)$$

and integrating between limits 0 to t and 0 to x

$$ln \frac{a}{a - x} = kIt,$$

or

$$x = a(1 - e^{-kIt}).$$

If the grains were of different sizes, the probability of their obtaining a nucleus would vary, the larger grains being more

[9] R. Slade and G. I. Higson: *Proc. Roy. Soc.*, **98A**, 154 (1920).

[10] G. I. Higson: "The Action of Light on the Photographic Plate," *Phot. J.*, **61**, 35 (1921), and *Ibid.*, p. 144.

[11] See p. 156, *loc. cit.*

[12] The. Svedberg: *Phot. J.*, **62**, 180 (1922).

[13] F. C. Toy: *Phot. J.*, **61**, 417 (1921).

[14] See p. 157, *loc. cit.*

likely to be affected; k would therefore have a different value for each size of grain.

"The present investigation has shown that k *has* a larger value for larger grains, but also that it is not generally true that the number of grains changed is a simple function of the product It. *It is therefore impossible that the mechanism of the process is the absorption of light in discrete quanta, as has been assumed above.**

"In this investigation of the photochemical law of the silver halide grain, plates were prepared from an emulsion containing grains which were, as nearly as possible, all the same size. The emulsion was coated on the plate in such a thin layer that there was only one layer of grains. These plates were exposed either to varying intensities for the same time or to the same intensity for varying times. The source of light used was monochromatic blue light from the mercury arc in some cases, and white light (continuous spectrum) in others.

"If the total number of grains present is a, and x is the number changed after exposure for a time t, to a light of intensity, I, then

$$\frac{dx}{dt} = P(a-x),$$

where P is the probability of any grain being made developable in unit time, and is a function of I and of t.

"Integrating

$$\int_0^x \frac{dx}{a-x} = \int_0^t P \cdot dt,$$

therefore

$$\ln \frac{a}{a-x} = \int_0^t P \cdot dt,$$

"This, however, does not make it possible to evaluate P as a function of I and t without making other assumptions."

But, although an equation of the type $x = c(1 - e^{-kIt})$ is de-

* Italics are ours.

ducible by application of the discrete theory of light,[15] it is also obtained by other considerations not involving this, but simply the assumption that the grains do differ in quality, *i.e.*, inherent sensitivity. The result, if confirmed, that the above expression did not hold, would not contradict the hypothesis of sensitivity-variation —it would only show that the distribution of sensitivity assumed[16] was inadequate. When Slade and Higson proceed still to evaluate

$$\int_0^x \frac{dx}{a-x} = \int_0^x \frac{dN}{N-n}\, as = \int_0^t P\, dt$$

where P is "the probability of any grain being made developable in unit time and is a function of I and t," it appears to us that they thereby assume tacitly, just the contrary to their statement (p. 158), "In the emulsion used . . . all the grains were of the same size, *and experimental proof has been obtained that they were all of the same quality.*"[17] It is difficult to see—on this basis, and accepting the principle that a grain made developable is completely developed (in three minutes, under their conditions with one-grain layers)—how *any* function of the type

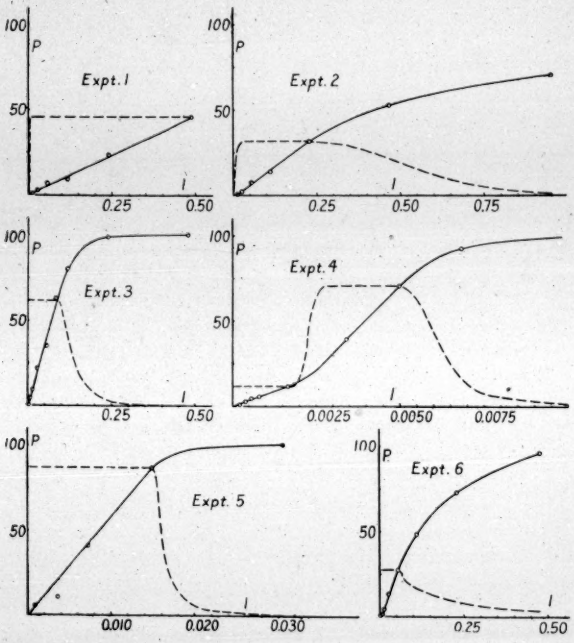
$$\int_0^x \frac{dx}{a-x}$$

could be evaluated. For all these grains, of identical size and "of the same quality" should become simultaneously developable for some one and the same exposure (although this unique exposure need not be that regulated by the reciprocity law $E = It$ = constant) *unless the mechanism of the process is the absorption of light in discrete quanta.* For, if grains of identical size *and quality* are exposed to radiation of discrete structure, then the "hits" will be regulated by some probability function.

[15] Cf. F. E. Ross: *Astrophys. J.*, **52**, 95 (1920).
[16] v. infra, p. 18.
[17] Our italics.

Since their premises, argument, and conclusions do not seem to fit together, it appeared desirable to reconsider their data from a different basis. Instead of forming the logarithmic quotient $ln\frac{a}{a-x}$

FIG. 1.

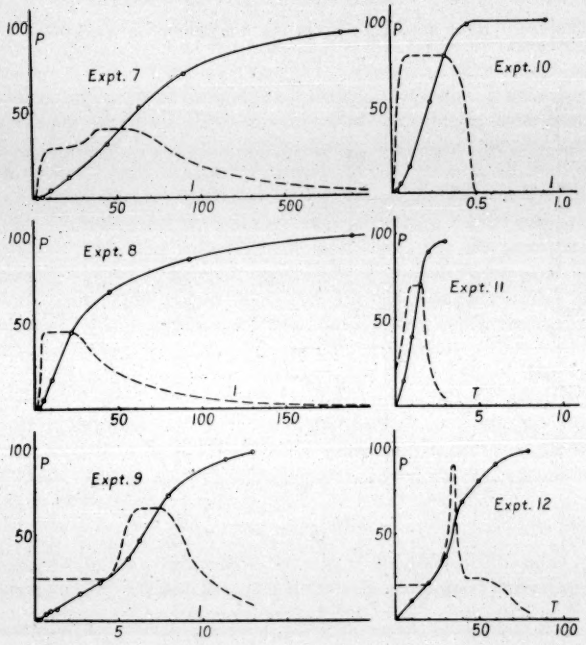


Slade and Higson's data replotted.

as dependent variable, which *assumes* either heterogeneity in the material or discreteness in the radiation—it is reasonable to plot the usual accumulation curve, *i.e.*, the number of grains changed, as ordinate, against either the *intensity*, for constant time of exposure, or the *time* for constant intensity. We have done this for Slade and Higson's data, with the results shown in Figs. 1, and 2, Intensity Scale.

In experiments 1, 2 and 3 (Fig. 1) (with monochromatic Hg. blue light) it will be seen that the number of grains changed is a linear function of the intensity up to 30 per cent. or more of the total, when the "rate of change" becomes less. To bring

FIG. 2.



Slade and Higson's data replotted.

out these features, we have also plotted the first derivatives of the curves, *i.e.*, as noted later, the "rate curves."

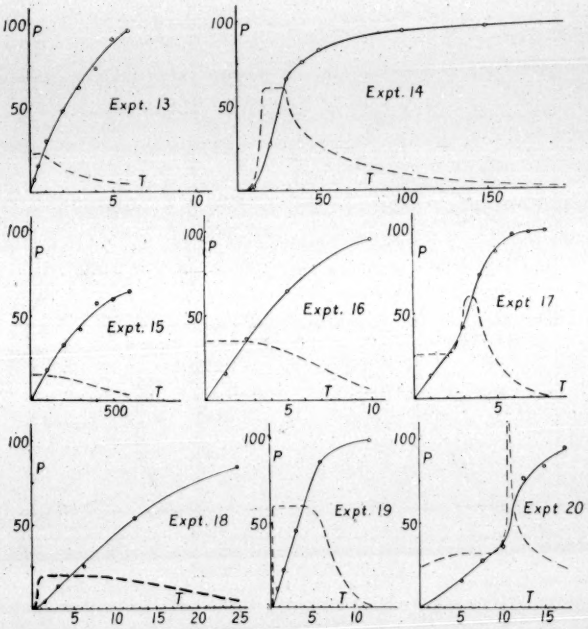
An interesting feature of these replotted curves is that the "white light" intensity curves show on the whole a greater similarity to the "monochromatic" time curves than to the "monochromatic" intensity curves. All of these show a well-marked "initial acceleration," corresponding to autocatalysis.

On the whole, the data agree with the view that the rate of photochemical change in the single grain, leading to a sufficient accumulation of the photoproduct to induce developability, follows a law of the type

$$\frac{dm}{dA} = k_1 A + k_2 f(m) A \ ,$$

where A = light absorbed, k_1 is the coefficient of absorption of

FIG. 3.



Slade and Higson's data replotted.

unchanged halide, k_2 is the coefficient of absorption of the photoproduct, $f(m)$ a function of its mass and distribution in the grain. Now we may suppose k_1 is small compared with $k_2 f(m)$, and that $f(m)$ varies initially from grain to grain. We can write

$k_2 f(m) = K$ and obtain the same type of "fundamental reaction formula" (for the single grain) as noted later, in which case the "first derivative" indicates the "frequency curve of inertias." *But* the present data do point to this "frequency curve" as not being entirely inherent, *i.e.*, preëxistent to exposure, but liable to be modified and induced by exposure itself, *as would result from an autocatalytic effect* of the photoproduct varying from grain to grain. Stress has been laid on this factor by one of the writers in a recent paper on the optical sensitizing effect of soluble iodides on the silver bromide emulsion.[18] Although in the subsequent portion of this paper it is neglected, the evidence from Slade and Higson's data, while not complete, decidedly indicates that this aspect requires further consideration. The more marked occurrence of the "initial acceleration" with both the "white light" intensity curves and the "monochromatic" time curves is perhaps connected with it; photosensitizing, for the same time period, but with different intensities, would be more probable with white light pulses than with the more regular trains of waves of "monochromatic" blue light, except when these were allowed to act for increasing periods of time.

In a paper on "The Photographic Efficiency of Heterogeneous Light,"[19] F. C. Toy has given incidentally results of further experiments tending to confirm Slade and Higson's formula as to intensity. He states,[20] "Slade and Higson have shown that the relation between light intensity, I, and the effect produced A, is given by

$$A = \alpha I(1-e^{-\beta I})$$

where α and β are constants, so that if the intensity is small, A varies as I^2." Later, he gives a table showing good correspondence between values of A calculated, and values observed.

These observations could be more valuable if the quantity A, termed "the photographic effect," were more precisely defined. It can only be presumed, in view of reference to their paper, that it refers to percentage number of grains made developable in a one-grain layer plate of grains of approximately equal size, and,

[18] *P. J.*, **62**, 89 (1922), "The Action of Soluble Iodides and Cyanides on the Photographic Emulsion," S. E. Sheppard.

[19] F. C. Toy: *Proc. Roy. Soc.*, A, **100**, 109 (1922).

[20] *Loc. cit.*, p. 110.

as assumed by Slade and Higson "identical quality." Since no statement as to this or other such effect is made, we cannot feel that this places Slade and Higson's formula beyond criticism; it does not seem to us compatible with Toy's own independent results, of the variable sensitivity of grains of the same emulsion, of the same shape and size. Neither a variable chance distribution of sensitizing nuclei, nor a quantum hypothesis of exposure gives such a relation, so that it remains in conflict with both types of hypothesis discussed here.

Under these conditions, an uncertainty cannot but be felt as to the conclusiveness of Toy's otherwise probable result "that over the spectral range used . . . radiations of different frequencies do not act independently in producing the photochemical change, but probably simply as a total amount irrespective of any difference of quality;" a result contrary to Slade and Higson's conclusion from their data that the same amount of energy as a monochromatic radiation has more photographic activity than as complex radiation such as "white light."

The existence of differential "sensitivity" amongst grains of the same size in one and the same emulsion was confirmed and extended to grains of the same geometrical shape by Toy.[21] Since his data did not extend below 30 per cent. developability, it is not profitable to compare the curve of *percentage* grains against *exposure* with Slade and Higson's results. It must suffice to point out again that this result does not seem to be compatible with the premises on which Slade and Higson found their formula.

II. TENTATIVE THEORY OF THE RELATION OF SENSITIVITY VARIATION TO THE CHARACERTISTIC CURVE.

The sensitometric characteristics of an emulsion are expressed in their entirety by the characteristic, or H. and D. curves, with the proviso, that the curves will possibly differ accordingly as an intensity or a time scale of exposures is impressed on the plate or film. If Schwarzschild's relations hold, they will differ only in the density ordinate by a common factor p and have the same form. The conclusions of Slade and Higson that intensity enters into the density-exposure function as I^2 for small values of I (and large values of t) and as I for large values of I (and small values of t) do not for the reasons cited appear to us conclusively proven.

[21] F. C. Toy: *Phot. J.*, **61**, 417 (1921).

Assuming, provisionally, that the incident energy is represented with sufficient accuracy either by It_e when t is constant, or by $I_e t$ when I is constant, then the sensitometric characteristics deducible from the curves are:

D_{max}	Maximum density developable
γ_∞	Maximum slope
i	Inertia if no regression occur
or a and b	Nietz's coefficients of the time-gamma convergence point
Lat.	Latitude
K	Velocity-constant of development

The empirical comparison of size-frequency curves with the characteristic curves and the derived values has only a limited value, however. It is desirable to have at least an orienting theory of the general relation of sensitivity-variation to the density-exposure function as a whole. We shall only assume at first that a statistical variation of sensitivity exists among the grains of the same emulsion, without prejudice as to its origin or explicit nature.

The conception of statistical variation among reacting units—*prima facie* of one chemical species—has not entered much into general chemical dynamics. Statistical variation of gas molecules as to velocity has been from the first, however, a feature of the kinetic theory of gases. Through statistical mechanics and radiation theory this has begun to react powerfully on the theory of chemical kinetics. While we may utilize conceptions developed in this field, notably by W. Mc. Lewis, R. C. Tolman and E. K. Rideal, it is in the field of biochemistry [22] that the application of variation to reaction velocity has been made most definite; this is most notable in regard to problems of the immuno-chemistry of cells and unicellular organisms. Biologically the existence of variation has to be admitted *de facto*, without, so far, any satisfactory theory of its origin prevailing.

Whether we are dealing with molecules, grains or cells as reacting units, variation of sensitivity (reactivity) amongst the units will greatly affect the course of the reaction, so that it may depend chiefly on this, and only secondarily upon the course of the fundamental reaction.

Now the actual progress of the reaction may be expressed graphically in two ways. First, as the usual accumulation or

[22] Cf. S. C. Brookes: *J. Gen. Physiolog.*, I, 61 (1918).

time curve, the amount changed being plotted as ordinate, against time as abscissa. For dispersed granules or cells, we could plot number x volume against time. There is also the rate curve, the ordinates being the amount of substance changed per unit time $\frac{\Delta x}{\Delta t}$ plotted against time. The former is the more usual in reaction kinetics, while the latter is the "mortality curve" of vital statistics. The latter curve is evidently the first derivative of the time curve, and we can pass from the *rate* curve to the *time* curve, either empirically by graphic integration, or algebraically, if the differential equation expressing the rate curve is known and integrable. Conversely we can obtain the rate curve from the time curve by differentiation.

Essential to the present argument is the fact that under certain conditions the *rate* (or mortality) curve may be identical with the variation (or frequency) curve of individual resistivities (inertias, reciprocals of sensitivities). Supposing the time curve replaced photographically by an exposure curve

$$D = f(E),$$

then with certain restrictions to be discussed, the first derivative of this

$$\frac{d D}{d E} = f'(E)$$

would give the variation curve of inertias of the reacting particles, or correlatively, the sensitivity-frequency curve.

The importance of the first derivative of the characteristic curve was first noticed by Nutting, Jones and Mees [23] for positive emulsions. It was introduced as dependent upon finite groups of grain sensitivities by Ross [24] in a theoretical discussion of the density-exposure function, and attention was a little later drawn to the subject in respect of negative emulsions by F. F. Renwick.[25] The latter's statement of the fundamental property of the derived curve appears to agree to a large extent with the conclusions reached here. "Since every ordinate of the derived curve represents the amount of silver bromide which has just attained the developable condition at the corresponding exposure, it is evident that we might regard each ordinate as a measure of the quantity

[23] *P. J.*, **54**, 342 (1914).
[24] *J. Opt. Soc. Amer.*, **4**, 255 (1920).
[25] *P. J.*, **61**, 10 (1921).

of silver bromide in the film having that particular true inertia value." It is now evident that if for "quantity" we substitute "number of particles per unit area" that the first derivative becomes the statistical frequency curve of inertias—provided there is no reduction of intensity through the film, as noted by Renwick, but also provided that the relation of grain size to grain sensitiveness is explicit.

Considerable modifications are necessary before these premises can be applied to actual sensitometric curves—obtained normally as

$$D = \phi (\text{Log } E),$$

with first derivative

$$\frac{d\,D}{d\,(\text{Log } E)} = \phi' (\text{Log } E).$$

To facilitate this application we have developed an approximate theory of the density-exposure function for very restricted conditions. The direct theoretical development of a function for the characteristic curve is beset with difficulty. Application of the calculus to a system composed of finite discontinuous units, such as silver halide grains, is itself contestable, and the difficulty becomes greater if statistical variation of the grain-sensitivities is admitted. The following device has been adopted for an indirect attack. A relatively simple photochemical reaction is assumed in an ideal homogeneous system. In the reaction equation obtained, the heterogeneity or variation factor is then introduced by replacing the reaction-constant of the function first obtained by various sensitivity or inertia variations.

The formula developed for photochemical change in a homogeneous layer is based on the Grotthus-Draper law that the rate of change is proportional to the energy absorbed by unchanged photolyte. The fundamental premise is therefore the same as that of Hurter and Driffield; no account is taken, however, of the absorption by altered silver halide for reasons discussed in a fuller paper. The expression obtained, for the general case of moderate absorption is:

$$e^{-K\delta x} = e^{-K\delta a} + (1 - e^{-K\delta a} e^{-KkI_a t}). \qquad (1)^{28}$$

[28] Deduction of this expression is dealt with in a fuller paper on this phase of the subject. J. Plotnikoff's integration (*Zeit. wissent. Phot.*, 19, 238 (1920)) of a similar differential equation leads to a different result and appears to us incorrect.

Where k = coefficient of absorption of supposed monochromatic radiation
δ = thickness of layer
a = original concentration of photolyte per unit volume
x = amount of photoproduct per unit volume

Before applying any considerations dealing with the heterogeneity of the actual system considered, we may note that this expression reduces to two much simpler forms:

(*a*) When the absorption factor $k\delta$ is very large:

Equation 1 may be written

$$ln \frac{[e^{K\delta x} - e^{-K\delta(a-x)}]}{[1 - e^{-K\delta(a-x)}]} = KkI_o t \qquad (2)$$

which, if $e^{-k\delta}$, approaches 0, becomes

$$ln (e^{K\delta x}) = KkI_o t$$

whence

$$\delta x = kI_o t \qquad (3)$$

a linear relation between amount of photoproduct and exposure.

(*b*) When the absorption factor $k\delta$ is very small, functions of the type $e^{-K\delta(\ )}$ can be expanded and reduced to:

$$e^{-K\delta(\ )} = 1 - K\delta(\ )$$

so that we have from equation 2

$$ln \frac{K\delta a}{K\delta (a-x)} = ln \frac{a}{a-x} = KkI_o t$$

$$x = a(1 - e^{K'I_o t}). \qquad (4)$$

This equation is of the so-called monomolecular form as found for the "dark reactions" and proposed by Elder for the density-exposure function. Its insufficiency *per se* for representation of this function has been exposed by Ross. According to present considerations, it could only be valid for a homogeneous material with very low absorption. The course of the reaction in such a homogeneous system may tend to approach either the linear form (equa. 3), when absorption is high (*e. g.*, the maximum of the wave-length sensitiveness curve) or the logarithmic form, when absorption is low (*e.g.*, the limits of the wave-length sensitiveness curve). But, in any case, photographic emulsions are heterogeneous systems.

Effect of Heterogeneity of Material.

We do not propose at this stage to consider the effect of modifying assumptions proper to the homogeneous reaction, *e.g.*, allowing for absorption by the altered silver halide, for limited autocatalysis by the photoproduct, etc.[27] It has appeared to us more important to proceed to consideration of sensitivity variation.

Consider the simplest case of sensitivity distribution, *viz.*, negligible deviation from a certain average value. The sensitivity-variation curve, corresponding to the rate curve, would be a straight line perpendicular to the abscissa. Its integral, the time curve, would, if the fundamental reaction is supposed uniform (of zero order), follow the axis to this point of intersection, then rise perpendicularly. That is, all grains would become developable at the same exposure, whatever the photochemical law for the single grain.

Apart from inherent and "quantum" sensitivity variations, in thick layers absorption of light in the upper layers involves an apparent gradient of sensitivity through the film. This is partly allowed for in the deduction of a reaction formula, which remains, however, of complicated form except for very high or very low values of the absorption factor. (See previous section.)

Following Ross, we may combine this absorption factor with inherent variation of sensitivity. Before resorting to this artifice it will be simpler to limit consideration at first to one-grain layers.

Suppose the photochemical absorption proper to be of such large or such small magnitude as to give the limiting cases obtained for the ideal reaction:

a. $x = kE$ Uniform rate

b. $x = a(1 - e^{-kE})$ Monomolecular rate

Then let us assume that the material is broken up into "micro-systems," each obeying one or other of the above formulæ, but in either case having different individual values of k—the velocity constant—distributed according to some probability function, *e.g.*,

[27] The changes in developability of the grain, with different developers, with solarization, with iodide, etc., are not consistent with so simple a view as that adopted, but these are secondary properties. The evidence from Slade and Higson's data (see p. 492), shows, however, that the possibility of autocatalysis being a primary factor requires further consideration.

the normal law of error. In either case, if k does not vary, all "grains" would become developable at the same exposure. We must then equate the actual rate to the distribution function of the k's—the sensitivity distribution. For immediate convenience in testing the "size variation" hypothesis of sensitivity, we have selected distribution functions of type found experimentally to represent our actual size-frequency data. The general progressive increase of "speed" with grain size shown in our data (p. 514) warrants such an attempt.

In general, if the granular material does not cover the whole of a given area, say 1 sq. cm., for which the reaction is being considered, the available exposure will be that falling on the normal grain surface or projective area, S, *i.e.*, according to previous considerations.

a. $$\frac{dx}{dt} = kI.S; \quad x = kS.E$$

b. $$\frac{dx}{dt} k'I.S(a-x); \quad x = a(1-e^{-k'SE})$$

provided the grains have the same sensitivities (or inertias), and $S = \sum_{o}^{n} s$, the sum of areas of n grains per sq. cm. Now we may obviously have two extreme cases for the function $k = f(i)$, the variation of inertia, in relation to size of grain. These are:

Case I.—$k = f(i)$, totally independent of grain size. Then, if the grains are the *same size*, integration has to be extended only to inertias, if of different sizes, to both inertias and grain sizes.

Case II.—$k = f(i)$ is a function of grain size. For example, the sensitivity may vary directly as the grain size, or the inertia be inversely proportional thereto. This is the simplest possibility, integration over a range of sizes being at the same time integration over sensitivities.

According to the argument developed, either of these cases may be conjoined with the fundamental "molecular" equations a or b. This procedure is developed, to illustrate the modifications, in the following synopsis:

EQUATION TYPE A.

	Fundamental reaction.	Variation function of inertias.	Size Condition.	Integral, or Exposure function.
	$\frac{dx}{dE} = k$	$k = y = y_0$	All same size	
I.	$\frac{dD}{dE} = k$	$f(i) = y = y_0$	S	$D = kEB\ s$
II.	$\frac{dx}{dE} = k$	$k = f(i)$	S	$D = s\int f(i)\ di$
		e.g., $f(i) = Be^{-ki}$	S	$D = Bs\int e^{-ki} di$
				$= Bs\int e^{-kE} dE$
				$= \frac{D_m}{k}\left(1 - e^{-kE}\right)$

NOTE.—A uniform rate of reaction, combined with an exponential inertia-distribution, gives the same type of density function (for constant grain size) as the "monomolecular" rate combined with uniform inertia-distribution. If the size of grain s varies, integration must be extended over $f(s)ds$ for the corresponding limits as $f(i)di$—which are not given unless the relation of i to s is explicit.

EQUATION TYPE B.

	Fundamental reaction.	Variation function of inertias.	Size Condition.	Integral, or Exposure function.
I.	$\frac{dx}{dE} = k(a - x)$	k constant	S same size	$D = D_m(1 - e^{-k'E})$
II.	$\frac{dD}{dE} = k'(D_m - D)$			
	$\frac{dD}{(D_m - D)} = k'\,dE$	$k' = f(i)$ $k'\,dE = f(i)\,di$	S	$\int \frac{dD}{D_m - D} = \int f(i)\,di$
				$\frac{1}{D_m} \ln \frac{D_m}{D_m - D} = (1 - e^{-ki})$
				$\frac{D_m}{D_m - D} = e^{\frac{D_m}{k'}(1 - e^{-k'E})}$
				$D = D_m(1 - e^{-u})$

NOTE.—This expression, $D = D_m(1 - e^{-u})$ which may be written

$$D = D_m\left[1 - e^{-D_m\int_0^E e^{-k'E} dE}\right]$$

has considerable similarity to that obtained by Ross (*J. Opt. Soc. Amer.*, **4**, 255 (1920)), *viz.*,

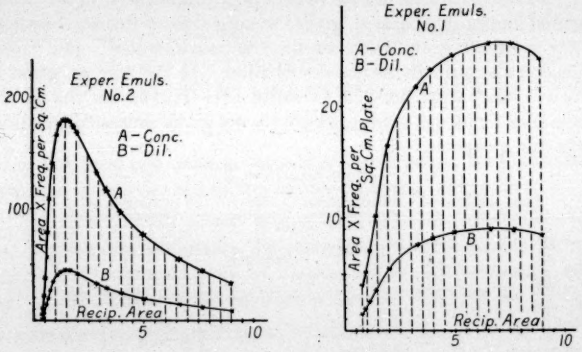
$$D = D_m \left[1 - \frac{1}{n} \sum_{p=o}^{p=n-1} e^{-kr^p E} \right]$$

where n is the finite number of classes of grains of different sensitivities supposed arranged in geometrical progression, p the sensitivity factor, r the ratio of sensitivities of different groups.

Relation of Size of Grain to Inertia.

On the "quantum" theory, as developed by Dr. L. Silberstein, the relation of "size of grain" to "inertia of grain" is apparently quite explicit. The projective-area of the grain, say s, is the measure of its chance of being hit by a quantum, hence, is the effective sensitiveness, statistically. On the other hand, the "size

FIG. 4.



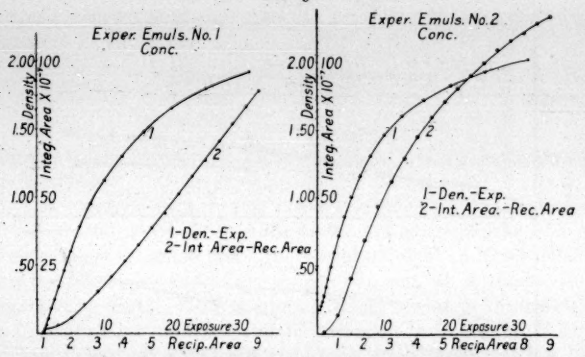
of grain" considered in this is not necessarily the "size" as found by the direct measurements of frequency, nor is the distribution function of sizes thus found directly available for the quantum theory, but requires some corrections for reasons noted later. We may, without immediate recourse to this theory, test empirically the hypothesis that the effective sensitivity of a grain is its "size"—to a first approximation, its "area." Then, the value of $f(i)$ in the foregoing synopses will be given by the distribution of *reciprocals* of the areas of the grains. On this

assumption, the relation of size of grain to inertia is explicit; if the reciprocal area-frequency (= inertia-frequency) per sq. cm. of plate be multiplied at each point by the area itself, the resultant curve should give, to a first approximation, the first derivative of the density-exposure function, when expressed in suitable units. Such curves are given in Fig. 1, as constructed from the original "frequency curve" for the two types of emulsion in question. They are each plotted for two cases,

A. For the total thickness of original plates;

B. For a one-grain layer.

FIG. 5.

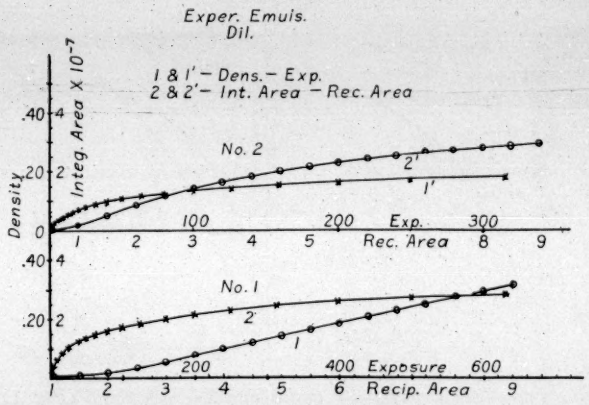


If now the curve No. 1, A and B, and No. 2, A and B (Fig. 4), are integrated graphically, the resulting curves should be comparable with the D-E curves. This has been done for both concentrated and dilute experimental emulsions and the results are shown in Figs. 5 and 6. It is obvious that for adequate comparison both abscissæ and ordinates should be expressed in the same units in both cases. The scale for the exposures is obtained from the condition that the maximum density must be reached with exhaustion of all classes of grains. For the density ordinates, the values 2 and 2′ in Figs. 5 and 6 should be multiplied by a factor for conversion of silver halide of a given grain to density, at same gamma as in Figs. 11 and 12. This correction will be applied when present work on the photometric constant is completed.

It will be seen that the "synthetic" curves give a "cut," as found by Renwick, but a very prolonged under-exposed region, and do not show very satisfactory correspondence with the actual sensitometric curves. The very prolonged "under-exposed" effect corresponds, however, to the fact that no allowance has been made for reduction of available light energy in the thickness of the film. With this correction it appears possible that the comparison may be improved.

Ideally, it would seem that the one-grain layer would be the

FIG. 6.



most satisfactory for comparison. The difficulty lies in the measurement of very small "densities"—of the order .002 to .20, with sufficient precision. Work on this is in progress, and a more satisfactory comparison will then be possible.

Experimental Data in Size-Frequency.

To determine size-frequency of grains in large amounts of emulsions we have developed methods of sedimentation and centrifugal fractionation.

For small amounts of emulsion, such as may conveniently be removed from a coated plate or film, we have developed a direct micrometric method. A "one-grain" layer of convenient distri-

bution is produced. Then by means of a high-power microscope, the particles are either photographed, or their outline drawn with a camera lucida. This stage is further enlarged by projection to a total of some 10,000 diameters, and the areas measured directly. For grains sufficiently circular, this is done by measurement of diameters, while larger polygonal grains are planimetered. The data are classified, and the size-frequency curves plotted. Eleven emulsions have already been analyzed in this way. They are enumerated below in Tables I and II.

Most of Table I is self-explanatory; the columns y_0, k and α have the following significance: It is found that the size-frequency curves of all emulsions can be represented by probability equations of two types:

$$\text{Exponential } f(s) = y = y_0 e^{-ks} \tag{5}$$

$$\text{Gaussian (modified)} \quad f(s) = y = y_0 e^{-k(s-\alpha)^2} \tag{6}$$

and the values given refer to the parameters of the corresponding equations.

It is worth noting here that previous estimates of the thickness of the grains of the silver halide in photographic emulsions have been in many cases too low. If, from the weight of silver halide and the number of grains per sq. cm. of plate, we determine the equivalent volume of the average particle, assuming the density to be that of pure silver bromide (the error in doing this is not greater than 3 or 4 per cent. even with fairly large amounts of iodide present), it is then easy to get the approximate thickness of the average grain (1) where the grains are spherical by determining their diameter

$$d = \sqrt[3]{\frac{6V}{\pi}}$$

and (2) where they are flat by dividing the average volume by the average projective area.

In two of the process emulsions studied which have almost entirely spherical grains this calculated diameter corresponds very closely to the average diameter determined statistically by the microscopic method. The third process emulsion (Process C), which is seen by examination of the photomicrographs to have a number of angular grains (usually indicating flatness) has a cal-

TABLE I.

Grain Characteristics—Average Size Grain.

Type of Film or Plate.	No. Grains per sq. cm. =N.	Gms. Ag-halide per sq. cm. of film of plate.	Per cent. Conc. Ag-halide per sq. cm. Emul. on plate or film.	Equiv. Diam. in μ.	Projective Area in μ^2.	Equiv. Vol. in μ^3.	Wt. in Gms. x 10^{12}.	Thickness in μ.	Ratio Thick:Diam.	Max. Grain Size Obs. in μ^3=M.	y_0	k	a
Process A.... (Lantern Slide)	4.30 x 10^8	0.000840	31.4	0.383	0.115	0.0301	0.195	0.386†	1: 1	1.2	4000.0	5.81	
Process B....	0.668 x 10^8	0.001366	33.6	0.844	0.560	0.317	2.05	0.846†	1: 1	1.6	340.4	8.95	0.555
Process C*...	3.08 x 10^8	0.001422	35.4	0.874	0.60	0.0711	0.46	0.710†	1: 1.2	3.2	286.7	4.72	0.630
Positive Emulsion....	1.853 x 10^8	0.000870	36.8	0.704	0.389	0.0726	0.47	0.187	1: 3.8	2.2	573.5	2.52	
Medium Speed A...	2.11 x 10^8	0.001213	33.4	0.757	0.450	0.0889	0.575	0.198	1: 3.8	6.2	1068.0	2.98	
Medium Speed B...	0.941 x 10^8	0.001300	32.5	0.799	0.502	0.213	1.38	0.124	1: 1.9	6.2	276.9	4.27	0.533
Medium Speed C...	1.50 x 10^8	0.001677	33.9	1.41	1.567	0.173	1.12	0.110	1:12.8	8.4	221.6 32.2	4.27 12.20	0.790 1.860
High Speed A...	0.656 x 10^8	0.001350	37.1	0.966	0.732	0.318	2.06	0.435	1: 2.2	8.6	110.2 310.9	0.953 3.36	
High Speed B ... Experimental	0.478 x 10^8	0.001470	33.7	1.67	2.198	0.467	3.08	0.216	1: 7.7	12.6	200.0 30.3	2.78 6.45	0.758 2.046
Emulsion No. 1 Experimental	5.690 x 10^8			0.	0.167					1.4	2375.3	4.75	
Emulsion No. 2	1.660 x 10^8			0.	0.710					2.8	235.2	3.06	0.575

*This is a panchromatic emulsion.
†Volumes assumed to be spherical.

TABLE II.

Sensitometric Characteristics.

Type of Film or Plate.	K	$\gamma\infty$	Approx. $D_{max.}$	a	b	Relative H. & D. Speed.			Latitude.		
						1 min.	3 min.	10 min.	1 min.	3 min.	10 min.
Process A (Lantern Slide)	0.354	4.05	7.5	0 to 0.05	0 to -0.27	6	6	7	7	9	3
Process B	0.429	4.95	6.2	$\bar{1}.90$	-0.35	6	7	8	2.3	3.6	2.0
Process C*	0.262	4.87	7.3	$\bar{2}.91$ to $\bar{1}.05$	-0.25 to -0.31	27	47	76	9	3.0	3.0
Positive Emulsion	0.384	4.82	5.1	$\bar{1}.82$ to $\bar{1}.92$	0 to -0.18	8	9	10	4	7	3.2
Medium Speed A	0.398	1.39	5.5	$\bar{3}.63$	$\bar{}$-0.32	366	729	918	316	316	316
Medium Speed B	0.352	1.23	4.2	$\bar{3}.78$	-0.15	439	763	856	282	200	200
Medium Speed C	0.323	1.62	5.7	$\bar{2}.00$	0	680	680	680	251	100	45
High Speed A	0.421	1.09	5.2	$\bar{3}.58$ to $\bar{3}.82$	-0.03 to -0.06	1236	1488	1560	178	159	71
High Speed B	0.321	0.932	3.7	$\bar{3}.15$	-0.05	2585	3820	4278	2510	794	398
Experimental Emulsion No. 1	0.254	2.42									
Experimental Emulsion No. 2	0.152	2.81									

* This is a panchromatic emulsion.

culated equivalent diameter somewhat smaller than the average projective diameter. For all the medium and high-speed emul-

FIG. 7.

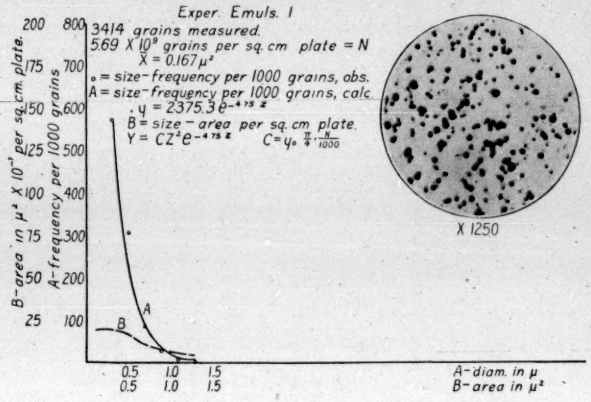
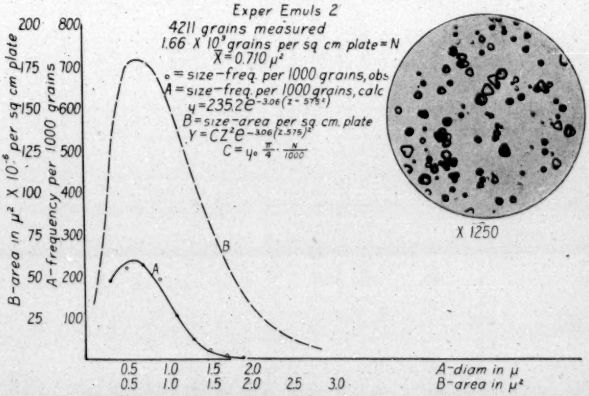

Exper. Emuls. 1
3414 grains measured.
5.69 X 10⁹ grains per sq. cm plate = N
X = 0.167 μ²
o = size-frequency per 1000 grains, obs.
A = size-frequency per 1000 grains, calc.
y = 2375.3 e^-4.75 z
B = size-area per sq. cm plate.
Y = CZ²e^-4.75 z C = y₀ π/4 · N/1000
B-area in μ² X 10⁻⁴ per sq. cm. plate.
A-frequency per 1000 grains
A
B
X 1250
0.5 1.0 1.5
0.5 1.0 1.5
A-diam. in μ
B-area in μ²

FIG. 8.


Exper Emuls 2
4211 grains measured
1.66 X 10⁹ grains per sq cm plate = N
X = 0.710 μ²
o = size-freq. per 1000 grains, obs
A = size-freq. per 1000 grains, calc
y = 2352 e^-3.06(z - 5.75²)
B = size-area per sq. cm. plate
Y = CZ²e^-3.06(z-5.75)²
C = y₀ π/4 · N/1000
B-area in μ² X 10⁻⁴ per sq cm plate
A-frequency per 1000 grains
A
B
X 1250
0.5 1.0 1.5 2.0
0.5 1.0 1.5 2.0 2.5 3.0
A-diam in μ
B-area in μ²

sions the calculations were made assuming the grains to be flat. The ratios of thickness to projective diameter are given in Table I.

Experimental Data on the Sensitometry.

The characteristic curves for the emulsions examined were determined in two ways:

FIG. 9.

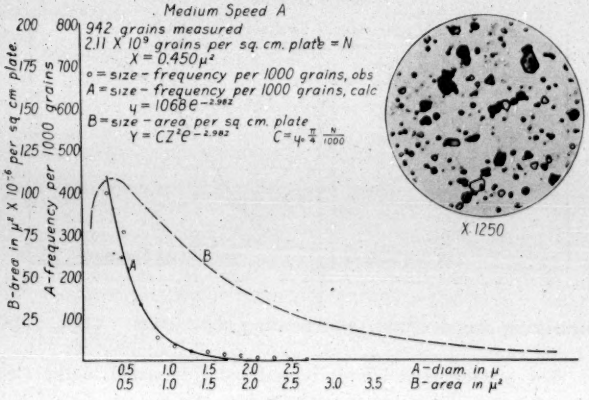
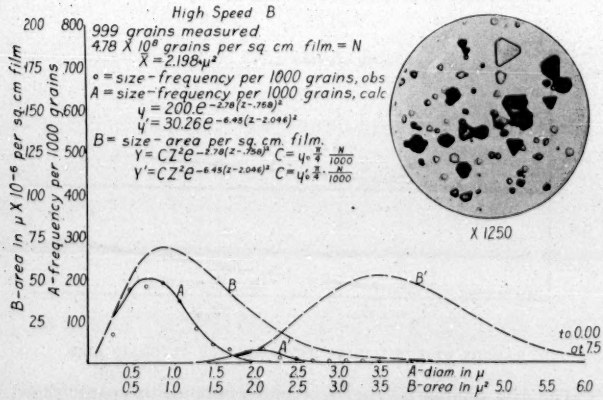

Medium Speed A
942 grains measured
2.11 X 10⁹ grains per sq. cm. plate = N
X = 0.450μ²
o = size-frequency per 1000 grains, obs
A = size-frequency per 1000 grains, calc
y = 1068 e^-2.982
B = size-area per sq. cm. plate
Y = CZ²e^-2.982
C = y₀ π/4 N/1000
B-area in μ² X 10⁻⁶ per sq. cm. plate
A-frequency per 1000 grains
A
B
X 1250
A-diam. in μ
B-area in μ²

FIG. 10.

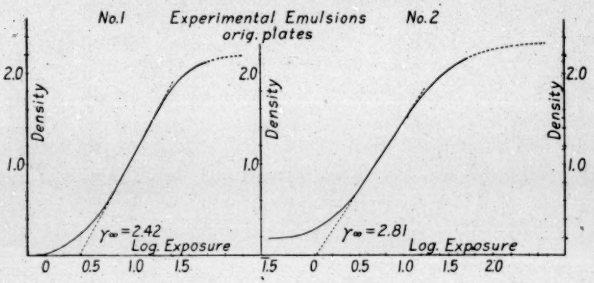

High Speed B
999 grains measured
4.78 X 10⁸ grains per sq cm film. = N
X = 2.198μ²
o = size-frequency per 1000 grains, obs
A = size-frequency per 1000 grains, calc
y = 200 e^-2.78(z-.758)²
y' = 30.26 e^-6.45(z-2.096)²
B = size-area per sq. cm. film.
Y = CZ²e^-2.78(z-.758)² C = y₀ π/4 N/1000
Y' = CZ²e^-6.45(z-2.096)² C = y'₀ π/4 N/1000
B-area in μ X 10⁻⁶ per sq. cm film
A-frequency per 1000 grains
A
B
B'
A'
X 1250
to 0.00 at 7.5
A-diam in μ
B-area in μ²

1. By intensity scales, using a Goldberg wedge and Higson's modification of Luther's crossed-wedge method. Curves for each

time of development were assembled, and the "family of curves" taken as giving the sensitometric data. (See Figs. 13 and 14.)

2. By time scale, using a Jones non-intermittent sensitometer,

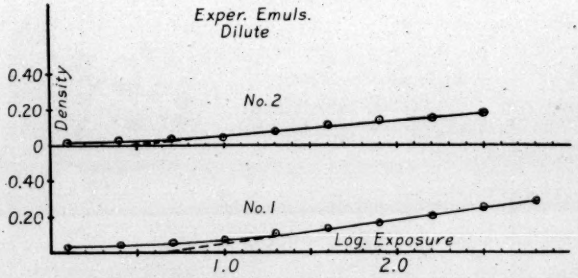
FIG. 11.



measuring the densities, and plotting the curves. (See Figs. 11 and 12.)

The sensitometric curves reproduced correspond to the frequency curves illustrated in Figs. 7, 8, 9, and 10.

FIG. 12.



III. NATURE OF SENSITIVITY AND RELATION TO GRAIN SIZE.

The data summarized in the second section of this paper show, as between different emulsions (mostly of the same fundamental type), a steady progression of "speed" with grain size. This

progression becomes more evident if the relative "speeds" are tabulated against maximum grain sizes.

FIG. 13.

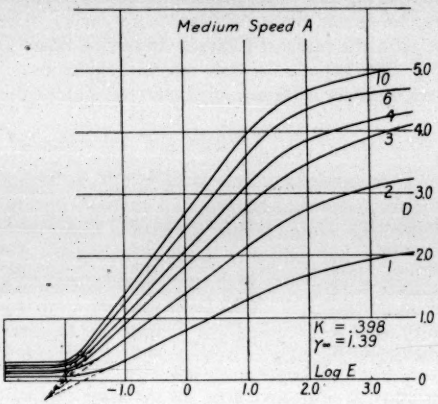
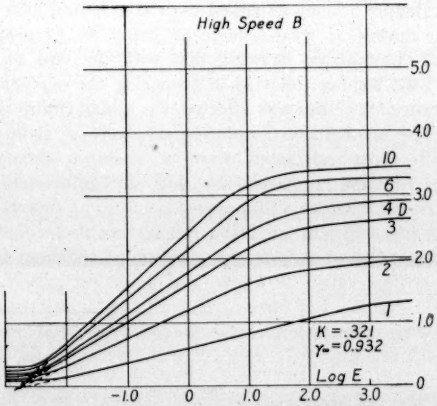


FIG. 14.



Since "speed" is obtained from a characteristic curve integrating the effects of grains of various sizes and sensitivities, in

several layers, we cannot, from this, obtain any idea of the quantitative relation of size to sensitivity. The hypothesis was used in the foregoing section, that the *inertia* of a grain was inversely as its projective area, that is, its probability of development directly as its area, to deduce the density-exposure curve. The lack of agreement with the measured curves cannot be taken at present as refuting this hypothesis, for reasons explained. A more direct attack consists in determining microscopically the relation

TABLE III.

Emulsion.	Rel. Speed (Maximum).	Maximum grain area in μ^2.
Process A (lantern slide)	7	1.2
Process B	8	1.6
Positive	10	2.2
Medium Speed A	918	6.2
Medium Speed B	856	6.2
Medium Speed C	680	8.4
High Speed A	1560	8.6
High Speed B	4278	12.6

of developability to projective area for the same exposure in one-grain layers.[28] This has been done by A. P. H. Trivelli and F. L. Righter.[29] They extended their counts and area measurements to clumps of from one to as many as 33 grains; well-confirmed observations showing that with the type of emulsion used, and the technic followed in preparing the one-grain layers, if one grain of a clump was affected, the whole clump is developable.[30] The results, noted immediately, were in striking agreement with those calculated from a quantum theory of the exposure function proposed by Dr. L. Silberstein.[31] This formula he obtained, to a first approximation, as follows: Let the necessary and sufficient condition for a grain to become developable be absorption of at least one quantum of sufficient frequency, above a critical value, as known in photoelectricity. Consider equal-sized grains. Let there be N grains upon an area A and let S be the projective area of each divided by A, and let n– light-

[28] Cf. The. Svedberg and H. Anderson: *Zeit. wiss. Phot.*, 1920, p. 36; *Phot. J.*, 1921, p. 325.

[29] *Phil. Mag.*, **44**, 252 (1922).

[30] Contrary to recent results of Svedberg.

[31] In the original paper a more rigorous deduction is given.

quanta impinge upon A—corrected for reflection, etc. To find q, the number of grains hit, the problem can be roughly treated as if N and q were continuous quantities.[31] At any stage the grains unaffected are $N-q$, the available fraction of area $S(N-q)$. Then for an increment dn of quanta

$$dq = S(N-q)dn$$

which gives

$$q = N(1-\epsilon^{-nS}).$$

(It will be noted that this makes $\frac{dq}{dn}$, the "sensitivity," directly proportional to S, the projective area, as assumed in section II.)

This simple formula implies that the cross-section of a light-quantum is small compared with a grain. If it be further assumed that only full incidence of a light quantum [32] is effective, and let r be the average equivalent radius of a grain, such that $S = \pi r^2$ and let ρ be the radius of the light quantum. Then the effective area of the grain [33] will be

$$S' = \pi (r-\rho)^2 = S\left(1-\frac{\rho}{r}\right)^2$$

so that the formula becomes

$$\frac{q}{N} = (1-\epsilon^{-\mu})$$

where

$$\mu = n S_1 = n S \left(1-\frac{\rho}{r}\right)^2$$

or if $\delta = \pi\rho^2$ be average area of cross-section of a quantum

$$\log\left(1-\frac{q}{N}\right) = -nS\left[1-\sqrt{\frac{\delta}{r}}\right]^2.$$

In Table IV the first column gives the number of grains in a clump, the second the average area s of a clump in square microns,

[31] The effect of wave-length is discussed in Dr. Silberstein's original paper.

[33] It should be noted that if instead of the total projective areas of the grains as the targets for the light quanta, we assume that the effective targets are silver nuclei in the grains then the quantum hypothesis can still be applied, provided that the areas of the nuclei are distributed in a constant ratio to the total grain area. But, of course, the effective energy acting in a given time per square cm. of plate would be quite different in this case as compared with Dr. Silberstein's original assumption. Energy measurements are being made in this Laboratory which should help to clear up this point.

the third the percentage of clumps affected out of all (N) clumps of each kind originally present, *i.e.*,

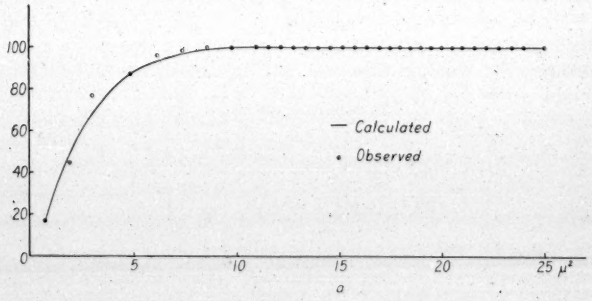
$$y = \frac{100\,q}{N}.$$

TABLE IV.

Clumps of	s in μ^2	y obs.	y calc.	Δy
1 grain	0.754	16.5	16.2 +	.03
2 "	1.925	44.9	48.4 —	3.5
3 "	2.03	76.6	68.9 +	8.3
4 "	4.88	87.1	87.3 —	0.2
5 "	6.18	96.0	93.3 —	2.7
6 "	7.42	98.2	96.4 —	1.8
7 "	(8.6)	100.0	98.0	2.0
8 "	(9.8)	100.0	99.6	0.4
9 "	(11.0)	100.0	99.8	0.2
10–31 "	(12.0)	100.0	100.0	0.0
32 "	> 24.	100.0	100.0	0.0
33 "	> 25.	100.0	100.0	0.0

The data are represented graphically in Fig. 15.

FIG. 15.



As stated earlier, this theory makes " sensitivity " entirely a matter of " effective projective area," *i.e.*, area of grain not shielded by other grains, and probability of being hit by at least one light quantum. A recent paper by The. Svedberg,[34] which has appeared since the investigations noted here were concluded, requires discussion in this connection. Svedberg has followed up the obser-

[34] *Phot. J.*, 1922, p. 186.

vation by M. B. Hodgson, of this Laboratory,[35] that development starts at one or more points of a grain. By interrupting development of grains exposed in a one-grain layer, he was able to count the number of "nuclei" thus revealed per grain for a larger number of grains of two size-classes (diameter $> 1.18\mu$ and $< 1.18\mu$). "Assuming that the product of light action, *i.e.*, the substance of the latent image, consists of small centres distributed through the grain, or through the light-affected part of the grain according to the laws of chance," a certain grain will become developed if it contains one or more than one developable centre. Now according to the laws of chance the percentage probability for the occurrence of n centres in a grain is

$$P_n = 100. \frac{e^{-\nu}\nu^n}{n!}$$

where ν is the average number of centres per grain. Thus the percentage probability that the grain will contain at least one centre is $P = 100(1 - e^{-\nu})$.

Svedberg's results confirm this formula and thereby the hypothesis of a chance distribution of centres. Now it is apparent that this result is in good agreement with the quantum theory just discussed. It is, however, equally accounted for by the alternative hypothesis of a photocatalyst formed in emulsification, and located in the grains according to chance. As regards the relation to size of grain, Svedberg's data only confirm the rapid increase of sensitivity with grain size. They are insufficient in range to correlate the sensitivity factor ν absolutely with either volume or cross-section, although it is pointed out that the results obtained differ, so far as they go, for light and X-rays, a *volume* relation being indicated in the latter case. This result would be more probable on the emulsification-nucleus theory than on the quantum theory, and therefore confirmation is important. Trivelli and Righter's results [36] indicate that the proportion of developable grains in a one-grain layer increases more rapidly, with increasing area, than provided by the simple formula

$$q/N = 1 - e^{-nS}$$

where S is the projective area, and using nearly monochromatic blue light of $\lambda = 480\mu\mu$. This might be interpreted in terms of an

[35] J. FRANK. INST., 1917, p. 705, 184.

[36] *Loc. cit.*

increase in number of centres more nearly proportional to the *volume;* on Silberstein's quantum theory, as already noted, it is accounted for by allowing a finite cross-section to the quantum of dimensions comparable to the area of the grain.

If we term E, the exposure, provisionally $= It$, ν the average number of nuclei per grain (due to emulsification plus exposure), then evidently for a one-grain layer

$$q/N = 1 - e^{-E\nu f(S)}.$$

Where $f(S)$ expresses the relation between ν and projective area of grain. If, on the simplest correlation discussed by Svedberg (and assumed provisionally by ourselves for "sensitivity," Sect. II) we put $f(S) = S$, we have

$$q/N = 1 - e^{-E\nu S}$$

which is of similar form to the simplest form of the quantum hypothesis

$$q/N = 1 - e^{-nS}.$$

The relations of these expressions to the density-exposure function are again of essentially similar type, initially. Silberstein [37] has pointed out that, assuming the simple formula above, for each class-size of an emulsion of type $\phi(S)$, where $\phi(S)$ is the equation of frequency distribution, the number of grains from s to $s + ds$ affected (at one quantum per grain) by n quanta will be $q_s ds$, where

$$q_s = \phi(S)\ [1 - e^{-nS}].$$

The total area of halide made developable will be found by integrating $q_s ds$ over the whole range of sizes, say from S_1 to S_2. Thus taking the exponential type of frequency curve $\phi(S) = Be^{-\mu S}$, from $S = S_1$ to S_2 where B and μ are constants, then the required integral or density value is

$$\Sigma = \frac{\beta}{(n-\mu)^2}\left\{1 + (n+\mu)S_1 e^{-(\mu+n)S_1} - [1 + (n+\mu)S_2]e^{-(\mu+n)S_2}\right\}$$

an equation which can be greatly simplified if $S_1 = 0$.

Formally, the same integration would apply to the equation derived from the "nucleus" hypothesis of Svedberg. It appears, however, that the actual range of "grain-areas" effective in the two cases would differ considerably. On the quantum hypothesis, for ordinary plates of several layers and high concentrations, the

[37] *Loc. cit.*

function $\phi(S)$ will not coincide with the size-frequency curve of that emulsion as determined by the methods discussed here. For, in the first place, if several grains form a contiguous clump, they may behave as *one grain* of class corresponding to their total projective area. Next, either a grain of a lower layer is shielded or not shielded.[38] If not shielded, it belongs to its proper class in one layer; if shielded it is reduced in class size to its unshielded portion. Hence, the effective size-frequency function $\phi(S)$ is not immediately determinable by mere counts, but has to be carefully corrected for the said factors. On the other hand, in the emulsification-nucleus hypothesis, the value S is the actually observed value in size-frequency determinations, and ϕ (S) the empirically determined size-frequency function. But, the correlation to n, that is, the exposure quantity (energy available or absorbed), requires in turn correction for diminution in passing through a multigrained layer. (See previous section II.) Hence it does not appear probable that a crucial distinction between the two hypotheses can be made on the ground of the integrated formulæ, since in either case mathematical refinements not immediately susceptible of experimental verification could be introduced making sufficient agreement with the actually measured density-exposure functions.

For physical optics, an experimental proof of the quantum hypothesis, of the discrete structure of light, is the issue. For photographic industry, if the "quantum" hypothesis is correct, the emulsion-maker has only to adjust the size-frequency curve of his precipitated silver halide, and ensure *absence* of inhibiting (desensitizing) substances in his gelatin to secure the maximum possible of speed, density, contrast, latitude, etc. If, however, the "emulsification-nucleus" hypothesis is correct, then the process of "sensitization" is of equal, or greater importance than that of grain-size determination; although at present apparently loosely coördinated with this, the possibility would exist of a more independent control of the two factors. In this connection, and as possibly helping to judge between the two hypotheses discussed, the phenomena of desensitizing are of great importance; particularly where it can be shown that the densensitizer has not been acting by mere destruction of the latent image as formed. In the subsequent paper certain independent evidence for the nucleus

[38] Cf. L. Silberstein, *loc. cit.*

hypothesis will be considered, as also the problems of densitizing, nucleus activation, and what has been termed by Lüppo-Cramer [39] the topo-chemistry of the silver halide grain.

SUMMARY.

1. The existence and nature of statistical variation of sensitivity among silver halide grains is discussed.

2. The relation of the statistical variation of sensitiveness, or inertia (its reciprocal), to the density exposure function is discussed. It is concluded that under certain conditions the first derivative of the density-exposure function will correspond with the intensity-variation function or curve.

3. The results of experimental determinations of grain-size-frequency curves are noted, and correlated with sensitometric data.

4. The decisive influence of the grain-size distribution and limits on the "speed" and other sensitometric variables is discussed in relation to the "quantum" and the "photocatalytic" theories of grain sensitiveness.

The Solvent Properties of Acetone. R. F. REMLER.—The paper takes up the following industrial consideration regarding acetone as a solvent: Uniformity of the present grade of acetone from calcium acetate, boiling point and volatility, freezing point, inflammability, dehydrating properties, miscibility with other solvents, use as a coupling or bending agent between immiscible solvents, relative test per gallon, physiologic effects and recovery. The solubilities of acetylene, cellulose acetate and cellulose nitrate, rosin and mineral oils, gums, resins, shellacs, animal and vegetable oils, fats and greases, waxes, asphalts, and bitumens, are discussed. Mention is also made of acetone in dry cleaning and leather industry, and as a constituent of paint, varnish, and carbon removers. (A. C. S. Abstract Service.)

Automatic Volumetric Analysis—Carbon Monoxide Recorder. HUGH S. TAYLOR and GUY B. TAYLOR.—An instrument for automatically making chemical analysis and recording the results is described. The instrument can be adapted to any case where two or more fluids can be mixed in regulated volumes, and the result of the obtained reaction of the fluids recorded by electrical conductivity, temperature rise, etc. Specifically the application of the apparatus to the analysis of flue-gas for carbon monoxide is described. (A. C. S. Abstract Service.)

[39] *Loc. cit.*

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, Ph.D.

Department of Chemistry, University of Chicago.

36. PERIODICITY OF TWO WITH RESPECT TO THE MEAN ISOTOPIC NUMBERS AND ATOMIC WEIGHTS.

THE periodicity of two which has been shown to appear in the atomic numbers, isotopic numbers, and abundance relations of the various atomic species, is found also in the mean values of the isotopic numbers, and therefore of the mean atomic weights when plotted against the atomic numbers. Figs. 8 and 10 show this periodicity particularly well. In the region of the light atoms up to atomic number 31 the isotopic number of an element of odd atomic number is in general one unit higher than when the atomic number is even. Strangely enough, among the elements of higher atomic number, practically all of the peaks which indicate a high isotopic number occur on atomic numbers which are even. Thus there is a reversal of the periodicity in this latter region. Up to atomic number 20 there is the sharp lower limit of 0 for the isotopic number, and this restrains the variation of this number to one direction. When the mean isotopic number rises sufficiently, it may vary in either direction, and in this latter case it is the even-numbered elements which have the higher isotopic numbers, and in a comparative sense, the higher atomic weights.

37. VARIABLES RELATED TO ATOM NUCLEI.

It has not been realized sufficiently that the variables used by the writer as the basis of his theory of nuclear structure and abundance, are all experimentally determined. In addition to the abundance (A) which has been used as the third dimension in the plots thus far given, there are five others which may be given in a two-dimensional diagram. These are the atomic weight (P), determined by both chemical and positive ray methods, and the atomic number, given both by the position of the element in the experimentally determined periodic classification of Mendelejeff, and by the X-ray method of Moseley. In addition to these there

* Continued from page 356, vol. 194, September, 1922.

are the three variables—N or $(P-M)$, n or $(P-2M)$, and the ratio N/P, all of which are given in terms of the two experimentally determined variables, so they are themselves determined by experiment. As only two of these variables are independent, it is obvious that all of them may be represented in a single two-dimensional diagram, but since, in such a plot, only two of the variables are found to be at right angles with each other, it seems valuable to use rectangular axes for each pair of variables in order to make the relations as obvious as possible. In this way ten two-dimensional diagrams arise. Each of these may be supposed to represent a three-dimensional plot in which the third axis gives the abundance (A) of each atomic species.

The ten diagrams are outlined in Table XXV.

TABLE XXV.

Outline of the Ten Two-dimensional Plots of the Variables P, M, N, n, and N/P, together with Equations representing Constant Values of the Variables.

(The ratio N/P is represented by R, and $(N/P)-0.5$ by R'.)

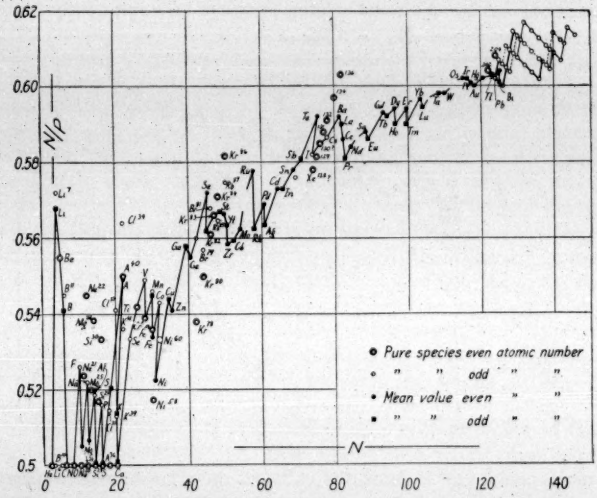
Figure.	Independent Variables	$R=k$. $R'=k'$.	$N=k$.	$P=k$.	$M=k$.	$n=k$.
5	P N	$N=PR$	$N=k$	$P=k$	$N=P-M$	$N=\frac{P+n}{2}$
6	M P	$P=\frac{2M}{1-2R'}$	$P=M+N$	$P=k$	$M=k$	$P=2M+n$
7	M N	$N=\frac{M(1+2R')}{1-2R'}$	$N=k$	$N=P-M$	$M=k$	$N=M+n$
10	M R'	$R'=k'$	$R'=\frac{N-M}{2(N+M)}$	$R'=\frac{P+2M}{2P}$	$M=k$	$R'=\frac{n}{2(n+2M)}$
8	P R'	$R'=k'$	$R'=\frac{2N-P}{2P}$	$P=k$	$R'=\frac{P-2M}{2P}$	$R'=\frac{n}{2P}$
15	N R'	$R'=k'$	$N=k$	$R'=\frac{N}{P}-0.5$	$R'=\frac{N-M}{2(N+M)}$	$R'=\frac{n}{2(2N-n)}$
16	n R'	$R'=k'$	$R'=\frac{n}{2(2N-n)}$	$R'=\frac{n}{2P}$	$R'=\frac{n}{3(2M+n)}$	$n=k$
9	M n	$n=\frac{4R'M}{1-2R'}$	$n=N-M$	$n=P-2M$	$M=k$	$n=k$
17	P n	$n=2PR'$	$n=2N-P$	$P=k$	$n=P-2M$	$n=k$
18	N n	$n=\frac{4R'N}{1+2R'}$	$N=k$	$n=2N-P$	$n=N-M$	$n=k$

Note.—All of the fifty lines for constant values in the ten figures are straight except eight, as can be seen from the equations.

The diagrams not already presented are given in Figs. 15, 16, 17, and 18.

Fig. 15, which gives the values of the relative negativeness (N/P) of atom nuclei plotted against the number of negative electrons (N) present, is very much like Fig. 8, which gives the same ratio plotted against the number of protons (P), except that in the former all of the peaks slope more toward the right.

FIG. 15.

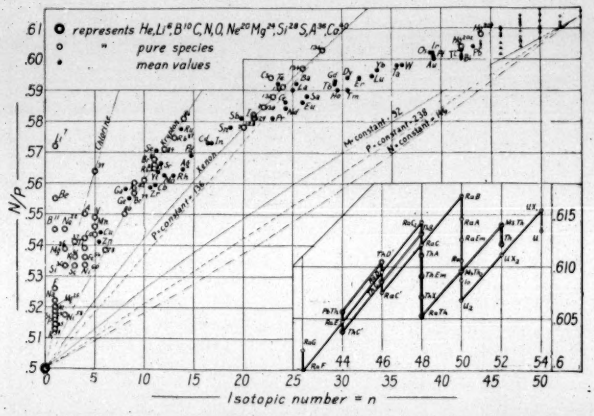


Figs. 17 and 18 are not very different in their form from Fig. 9 already given. The great similarity of the figures which relate any one variable to M, to P, and to N, is an illustration of the very simple relations which exist in a general way between these three variables.

Fig. 16 illustrates the increase of the relative negativeness (N/P) of the nuclei as the isotopic number increases. This plot has the interesting characteristic that all of the very abundant atomic species, with the exception of iron and aluminium, are represented by the *single point* at the origin. Thus 93 out of 100 of the atoms in the earth's crust are represented by this point.

The region of highest stability has very nearly the form of a parabola, and along any neutronal line (n = const.) the stability decreases on passing vertically higher or lower out of this region. As an example, the lines showing the net nuclear charge as 92, the number of positive electrons as 238, and the number of negative electrons as 148, which are the values for ordinary uranium, are given. These lines indicate that for a nucleus with any of these three properties, represented by relatively large numbers, to exist, the isotopic number must increase to a sufficiently high

FIG. 16.



value (about 54) to cause the value of the relative negativeness to become sufficiently high (about 0.614) that the repulsion due to the large net positiveness may be thereby overcome.

The diagram in the lower right-hand corner of Fig. 7 indicates that during alpha disintegrations the isotopic number remains constant while the relative negativeness increases slightly. After several changes the nucleus becomes so negative in the relative sense that positively charged particles no longer leave it, but negative electrons are shot off. Each beta disintegration lowers the isotopic number by two, and in this region decreases the relative negativeness slightly more than two alpha disintegrations have increased it, as has been pointed out in an earlier section of the paper.

38. FUNDAMENTAL PRINCIPLES FOR THE PREDICTION OF ISOTOPES FROM THE CHEMICAL OR MEAN ATOMIC WEIGHTS.

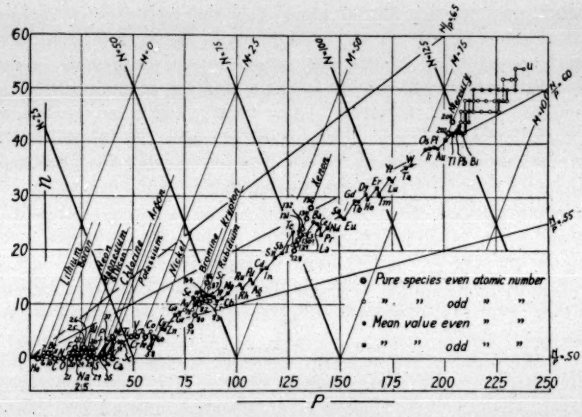
A number of recent papers have made extensive predictions as to just what isotopes exist, but in every case all of these, except those made by the writer, have violated some of the fundamental relations of nuclear stability and abundance as presented in the earlier sections of the present paper, and so have not been justified by the later discoveries. Thus one writer predicted that all pure atomic species would be found to have atomic weights which are even numbers, and that fluorine, for example, would be found to be a mixture of isotopes of atomic weights 18 and 20, while another predicted that lithium would be found to consist of isotopes of atomic weights 5 and 7. The first of these predictions is at variance with one of the most important of the general atomic weight relations and did not need the findings of the positive ray method to show its falsity. The latter violates an even more general relation, but is more excusable, since the lithium nuclei are the simplest of all of the complex nuclei other than the basic alpha particle, so it might be *possible* that it would not follow the general relations, which indicate that the atomic weights should be 7 and 6, as predicted by the writer. Since the examples given above are only a small fraction of the erroneous predictions, it seems advisable to list below the most important general relations which seem to determine the existence or non-existence of atomic species.

Before doing this it seems advisable to call attention to the fact that the positive ray method, while it gives very remarkable results, should not be considered to be an infallible guide in determining just what isotopes exist, since at its present stage of development it will err in not finding those isotopes which exist in small percentages. Just what its limit of detection is, does not seem to be known, but it is probable that percentages equal to 1 or less per cent. are practically certain to be missed. It should also be kept in mind that the mathematical theory of the stability of a system so complicated as a complex nucleus is exceedingly involved, and that small changes in the number of nuclear electrons and protons may be expected to produce in some cases very great changes in stability, especially when the number of particles is small. Therefore all that can be expected of a theory is that it will point out correctly the general system, but it must not be

expected that it will be able to give the details in every specific instance.

At the present time the greatest uncertainty which exists in this connection is that concerning the magnitude of the "packing effect" during the formation of more complex nuclei as compared with that which occurs in the formation of the helium atom from hydrogen. The approximate constancy of the packing effect as expressed by the *whole number rule* of Harkins and Wilson (1915) has already been discussed.

FIG. 17.



The principles to be kept in mind in the prediction of isotopes are:

1. A deviation of the atomic weight on the oxygen basis from a whole number which is more than two or three-hundredths of a unit greater than the experimental error, may be considered as a basis for the prediction of isotopes, particularly among the light atoms. The exact limits within which the atomic weight of a pure atomic species may vary from a whole number are still to be determined experimentally, but they are evidently very small.

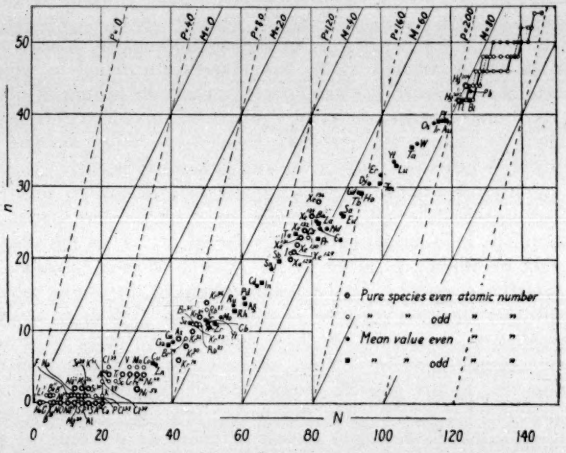
2. Among the light atoms an element may be considered, provided complicating factors are absent, to consist essentially of *one* atomic species if its atomic weight is the whole number given

by the more complete form of the Harkins-Wilson atomic-weight equation:

$$P = 2(M + f) + \tfrac{1}{2} + [(-1)^{M-1} \times \tfrac{1}{2}]$$

in which f is 0 up to atomic number 17, and is 2 between atomic numbers 22 and 27. On this basis helium, carbon, nitrogen, oxygen, fluorine, and sodium would be considered as single species. Also titanium, vanadium, chromium, and manganese are indicated by their atomic weights as nearly pure species in each case. While this relation alone might seem to indicate that beryllium of atomic

FIG. 18.



weight 9, should consist of isotopes of atomic weights 8 and 10, the writer in 1915 considered that in this element a certain complicating factor is present, and that beryllium is a *single species* of atomic weight 9. This was found to be correct, for in 1921 G. P. Thomson discovered that beryllium is probably a simple element. The writer had concluded that the atomic-weight equation given above, developed on the basis of the idea that the principal isotope of a light element of even atomic number has a nucleus which is built of alpha particles alone, or these particles with two cementing electrons, could not be expected to apply

to beryllium. Thus while 3, 4, 5, 6, 7, 8, 9, or 10 alpha particles may hold together, it seemed probable that a third particle or group, aside from the two alpha particles in the beryllium nucleus, would be necessary to make a stable nuclear compound. From this viewpoint [37] it was assumed that the single atomic species had a nucleus of the formula a_2pe. Thus the beryllium nucleus may be considered to consist of two alpha particles and one neutron. The case of scandium will be treated in a later paragraph.

3. No isotope for which the value of N/P is less than $\frac{1}{2}$, should be predicted. For example, as has been stated, one writer predicted that lithium would be found to consist of isotopes of atomic weights 7 and 5. Now the value of N/P for the latter of these two isotopes is $2/5$, an entirely improbable value, since no species of complex atoms has as yet been found in which the value of this ratio is less than $\frac{1}{2}$. Even the helium of mass 3, as found *experimentally* by Rutherford, in which this ratio seemed to be $1/3$, has now been found to be fallacious and to actually be helium of mass 4, in which the ratio is $\frac{1}{2}$.

4. The probability of the existence of a detectable quantity of an isotope is small if the value of N/P for the species is abnormally high for its particular value of M. Thus the atomic weight of lithium, as given by the Harkins-Wilson equation, is 7, which has proved to be the atomic weight of the isotope which constitutes about 94 per cent. of the element. The mean atomic weight, 6.94, indicates that there must be an isotope of lower atomic weight present. Now, according to principle 3 given above, the lowest possible atomic weight for this element of atomic number 3 is 6. On this basis the writer predicted that lithium would be found to consist of about 94 per cent. of an isotope of weight 7, with 6 per cent. of weight 6. The existence of these two isotopes was determined experimentally about a year later by G. P. Thomson and by Dempster. Rutherford had predicted the existence of isotopes of weights 6, 7, and 8. Now it may be possible that an isotope of weight 8 may exist, but the value of N/P for this atomic species is 0.625, which is higher than that for any known atomic species, and is entirely abnormal in the region of the light atoms, so it is not surprising that it was not revealed in the experiments.

[37] *Proc. Nat. Acad. Science*, **2**, 216–24 (1916); *J. Am. Chem. Soc.*, **39**, 856–60 (1917).

5. *Elements of Even Atomic Number.*—These should be divided into three classes: Light elements up to atomic number 26 or 28; heavy elements between atomic numbers 30 and 82, and radioactive elements of atomic numbers 82 to 92.

In all of these regions the most abundant isotopes will in general be those whose atomic weights are *even numbers,* and which at the same time have such values of N/P as give the highest abundance. Among the light atoms up to atomic number 16 the most abundant isotope has the isotopic number 0, between atomic numbers 18 and 30, with the exception of calcium (20), and nickel (28), it has the isotopic number 4. Thus in zinc the most abundant isotope has the isotopic number 4, and the abundance falls off as the isotopic number rises above this value. As the isotopic number of the most abundant isotope rises above 4, it may be expected that the isotopes will be distributed more evenly on both sides of the most abundant isotope, that is with both higher and lower isotopic numbers, but not with entire symmetry.

In general isotopes whose atomic weights are divisible by 4 will be more abundant than those divisible by 2 but not by 4, particularly in the region of the light atoms. As the atomic number increases this distinction may be expected to die out more and more.

Just what atomic species of even atomic number and odd atomic weight exist, it is difficult to predict, but they may be expected to be in general less abundant and less numerous than those of even atomic weight, and also in general to lie between the latter. *Thus in almost all of the cases thus far investigated isotopes of even atomic weight form the two extremes,* as 20 and 22 for neon, 24 and 26 for magnesium, 36 and 40 for argon, 40 and 44 for calcium, 58 and 60 for nickel, 64 and 70 for zinc, 78 and 86 for krypton, 116 and 124 for tin, 128 and 136 for xenon, etc.

In the region of the light elements there are not more than two isotopes of even atomic weight, but in the region of the heavy elements about 4 or 5 such isotopes may be expected. The total number of isotopes will be greater than this by the number of isotopes of odd atomic weight.

6. *Elements of Odd Atomic Number.*—While the relations for the isotopes of even atomic number are thus quite complex, *those for isotopes of odd atomic number are much more simple,*

not because the number of possibilities is less, but merely because the number of isotopes which are sufficiently abundant and stable to be apparent, is considerably less.

Thus the relations to be expected from the general theory *in the case of elements of odd atomic number* are: (1) Isotopes few in number in comparison with the elements of even atomic number; (2) isotopes mostly of odd atomic weight. In addition to this it is probable at least, so long as the atomic number does not become too high (which tends to level out contrasts of all sorts), that (3) members of the lithium series in general are more abundant than those of the meta-chlorine (beryllium) series.

In accordance with these principles it is to be expected, if the mean, or chemical, atomic weight is precisely known, and is very close to an odd whole number, that *the element consists of one pure atomic species,* or else mostly of one pure atomic species mixed with very small amounts of others. The most accurately known element weights of odd-numbered elements in the region of abundant isotopes (elements 28 to 81), are bromine, 79.92, iodine, 126.92, and silver, 107.88. Thus the mean atomic weight of bromine is 80 within the limits of error. If this were an odd number it would indicate the probability that bromine is wholly or almost wholly one pure atomic species. However, since it is an even number it indicates just as strongly that bromine is a mixture of two isotopes, 79 and 81 in atomic weight, and in nearly equal percentages. The atomic weight of iodine, on the other hand, is an odd number, 127, which indicates that it consists of only *one* atomic species.

"According to the above principles silver should consist either wholly or mainly of isotopes of atomic weights 107 and 109, rubidium of atomic weights 85 and 87, copper 63 and 65, and ruthenium of a single species mostly of weight 103, provided the chemical atomic weights are as precise as they are supposed to be. The general predictions are easily applied to the elements of even atomic number."

In accord with the prediction in regard to rubidium given in the last paragraph, as sent to the *Philosophical Magazine* in February, 1921, the isotopes of this element have been found by Aston to be two in number and to have the predicted atomic weights. The isotopes of lithium, atomic weights 6 and 7, were correctly predicted about a year before they were discovered, and

those of boron, 10 and 11, several months before they were found.[38] In general the predictions have been verified in a remarkable way, especially since all of the *general* principles upon which they were based were published before any isotopes, other than those of neon and in the radioactive region, had been discovered. Thus three general predictions were verified by Dempster's discovery of the isotopes of zinc. These were:

1. That the region of abundant isotopes would begin at about atomic number 28. This prediction was made in 1915, and it was found in 1921 that zinc (at. no. = 30) is the first element in which the number of isotopes rises to 4.

2. That the number of isotopes would be large in this region for elements of even atomic number, not in general for those of odd number.

3. That the atomic weights would be even numbers in general for elements of even atomic number.

In December, 1920, Dempster reported to the Physical Society[39] that his preliminary results on the isotopes of zinc showed that their atomic weights were 63, 65, 67, and 69, and called the attention of the writer to the fact that these weights were not in accord with relation 3 listed above. The writer replied that he was confident that when the atomic weights were determined more accurately they would be found to be either 62, 64, 66, and 68, or else, more probably taking into consideration the probable N/P values in this region, 64, 66, 68, and 70. That the supposition was justified was proved by Dempster's more accurate final results, which proved to give the four numbers given last.

In a plot entitled "A General System of the Isotopes,"[40] drawn in December, 1921, the writer listed the most probable isotopes of the elements of odd atomic number, and what he believed would prove to be in general the most abundant isotopes of the elements of even atomic number—that is, those of even atomic weight. No attempt was made to predict those isotopes of even atomic number which have an odd atomic weight. The isotopes of tin listed were those of atomic weights 116, 118, 120, 122, and 124, and these were found later by Aston to be respectively third, second, first,

[38] Harkins: *J. Am. Chem. Soc.*, **42** (1920), presented in April, 1920.
[39] Pages 147–8, Aston's "Isotopes" (1922).
[40] Fig. 21 of the present paper.

seventh, and fourth in abundance among the isotopes of this element, and thus included *all* of the four most abundant isotopes. While tin has several isotopes of odd atomic weight they are relatively unimportant so far as abundance is concerned. Their atomic weights and relative abundance are: 117 (sixth), 119 (fifth), and 121 (eighth).

It is of interest that the most abundant isotope of zinc, of krypton, and of tin, all have atomic weights which are divisible by 4. Xenon, according to Aston's preliminary results, is exceptional in that its most abundant isotope has an odd atomic weight.

39. THE ALPHA PARTICLE AS THE MOST ABUNDANT ELECTRON GROUP, AND FURTHER EVIDENCE THAT ATOM NUCLEI ARE BUILT UP MOSTLY FROM ALPHA PARTICLES.

TABLE XXVI.*

Formulæ Expressing the Atomic Weight and Nuclear Positive Charge of the Light Atoms of Even Atomic Number.

(Most abundant isotope only.)

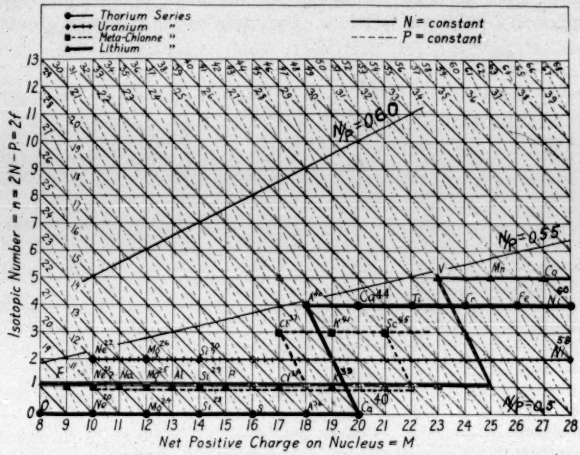
Atomic Number.	Element.	Nuclear Formula.	Atomic Number.	Element.	Nuclear Formula.
6	C	a_3	18	A	$a_{10}e'_2$
8	O	a_4	22	Ti	$a_{12}e'_2$
10	Ne	a_5	24	Cr	$a_{13}e'_2$
12	Mg	a_6	26	Fe	$a_{14}e'_2$
14	Si	a_7			
16	S	a_8			
18	(A)	(a_9)			
20	Ca	a_{10}			

*This table is similar to Table III, the difference being that Table III was prepared from the mean atomic weights before the discovery of the isotopes involved.

The first part of the present paper gave strong evidence from the standpoint of the *mean atomic weights* and the abundance of the elements (see particularly Tables III, IV, and XII) that all atom nuclei, other than that of hydrogen, are built up mostly from alpha particles. The present section will show that the atomic weights and the abundance relations of the individual atomic species, taken in connection with what has been presented before, make the evidence entirely conclusive. The tables and the figure of this section were prepared in order to prove that the Rutherford theory, that the light atoms are built up mostly of particles of mass 3, was not justified. From this standpoint the presentation here is unnecessary, since Rutherford has recently withdrawn his theory.

Table XXVI, which gives formulæ that express the atomic weight and nuclear charge of the most abundant isotope for all of the light elements of even atomic number, is of extreme interest.

FIG. 19.


Thorium Series
Uranium "
Meta-Chlonne "
Lithium "
N = constant
P = constant
Np=0.60
Np=0.55
Np=0.5
Isotopic Number = n = 2N − P = 2Y
Net Positive Charge on Nucleus = M
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28

Each corner where 4 lines meet represents a *possible* isotope. The interesting feature of the plot is that only certain corners represent *actual* isotopes, and these exhibit a more or less definite pattern. The heavy line from Ni^{28} to O has exactly the characteristics found in a similar plot of the thorium disintegration series. To the left of O the series extends two atomic numbers to carbon, and from Ni^{4} it extends two atomic numbers to the right to Zn^{+4}. Of the 16 atomic species in this series all but one (K^{+9}, which would be unstable) have been discovered. This plot gives *definite* evidence of the fundamental importance of alpha particles in the building of light atoms, since along the heavy horizontal lines the difference between two adjacent atomic species with respect to composition is that of one alpha particle.

This table expresses *the remarkable fact that for the six successive elements of even number, carbon, oxygen, neon, magnesium, silicon, and sulphur, the most abundant isotope has both a charge and a mass equal to a whole number times the charge and mass of the alpha particle.* With argon there is a slight irregularity in that the less abundant isotope meets this condition, while the adherence to the rule returns again in calcium. The elements of higher atomic number, titanium, chromium, and iron (and presumably nickel, 60, and zinc, 64),[41] show the same general rela-

[41] *Phil. Mag.*, **42**, 332 (1921). Since this was first written nickel, 60, and zinc, 64, have been discovered.

tionship except that each nucleus contains two negative (cementing) electrons in addition, so there is also present in each case one alpha particle in excess of that required to give the nuclear charge; while the mass is still expressed by that of a whole number of alpha particles. This corresponds to the presence in these nuclei of a quadruple neutron, which may be called a helio group,

TABLE XXVII.

Atomic Percentage of Atomic Species in Meteorites, Showing the Importance of the Weight 4.

Atomic weight	4q	3q	4q not 3q	3q not 4q	4q+3	4q+2	4q+1
Element.							
Carbon	0.12	0.12	...	...	...	....	...
Oxygen	53.16	...	53.16	...	...	...	...
Sodium	0.62	...	0.62	...	0.62	...	...
Magnesium	9.86	9.86	...	...	...	1.65	1.65
Aluminium	...	1.21	...	1.21	1.21	...	...
Silicon[28]	13.82	...	13.82	...	...	...	1.38
Phosphorus	...	...	...	...	0.06	...	...
Sulphur	1.46	...	1.46	...	...	...	...
Potassium	...	0.11	...	0.11	0.11	...	...
Calcium	0.97	...	0.97	...	...	...	...
Titanium	0.005	0.005	...	...	...	...	...
Chromium	0.13	...	0.13	...	...	...	...
Manganese	...	...	...	...	0.06	...	...
Iron[56]	12.30	...	12.30	...	...	...	...
Cobalt	...	...	...	...	0.04	...	...
			82.46	1.32	2.10	1.65	3.03

of the formula p_4e_4, where p represents a hydrogen nucleus or proton, and e a negative electron. The two cementing electrons correspond exactly in their function to the beta electrons which are shot off in pairs, but not simultaneously, in the radioactive disintegration series. Fig. 19, which is an enlarged section of Fig. 5, shows that Zn_4^{64}, Ni_4^{60}, Fe_4^{56}, Cr_4^{52}, Ti_4^{48}, Ca_4^{44}, A_4^{40}, K_2^{40}, Ca_0^{40}, A_0^{36}, S_0^{32}, Si_0^{28}, Mg_0^{24}, Ne_0^{20}, O_0^{16}, and C_0^{12} show exactly the form of a radioactive disintegration series. Of all of these atomic species, K_2^{40}, which is the one which should according to the theory be extremely unstable, is the only one which remains undiscovered.

It is remarkable that the few atomic species of this series shown in Fig. 19 make up 93 per cent. of the material of the

meteorites, and nearly as great a percentage of the surface of the earth, which fact, when combined with the fact that the relations are exactly those of the thorium disintegration series, seems to the writer to be conclusive evidence that the alpha particle is the principal group concerned in atom building, in the region of the light atoms as well as in that of the radioactive atoms.

In addition Fig. 19 shows that Co, Mn, V, K_1^{39}, Cl_1^{35}, and P_1^{31}; Ni_2^{58}, Mg_2^{26}, and Ne_2^{22}; and also Sc_3, Sc_3^{45}, K_3^{41}, and Cl_3^{37}; K_3, and Cl_3 form three other similar series in that they have just the spacing due to alpha particles.

That the weight 4 is of extreme importance is shown clearly by Table XXVII, which gives the abundance of the atomic species in the meteorites. In the table q represents a whole number.

The totals of the columns in a similar table for the earth's crust are almost the same, except that the column $4q + 3$ adds up about 8 atomic per cent., and therefore is much more prominent. In both tables the abundance of the atomic species whose atomic weights are divisible by 4 is much greater than that of those divisible by 3, and the latter seems to gain its relative importance only through the inclusion of those weights which are common to the column $4q$.

(To be continued.)

Diffusion of Certain Metals into Zinc.—At the recent (forty-second) meeting of the American Electrochemical Society, Walter G. Traub, of the senior class in Chemical Engineering, University of Wisconsin, presented a communication embodying some experiments that show that thin deposits of gold, silver, copper and brass electroplated on zinc will in time disappear, having been diffused into the zinc. Nickel does not appreciably diffuse, and, therefore, by previously coating zinc with nickel the diffusion of the other metals is prevented. These results are in extension of results that are recorded by Roberts-Austen. The subject of diffusion of two solid metals is discussed in some detail in his work on metallurgy. See, for instance, "Introduction to the Study of Metallurgy" (fifth edition, 1902, pp. 66–73). The old process of making steel is an example of the interpenetration of solids. That some of the common metals, especially those of low melting points, give off appreciable vapors at ordinary temperatures has long been known. These vapors will affect a photographic plate, the action being entirely different from that of radioactivity. Some experiments in this direction, by Leffmann, are recorded in this JOURNAL (1914, vol. 178, p. 743). H. L.

The Straggling of Alpha Particles by Matter. G. H. HENDERSON. (*Phil. Mag.*, July, 1922.)—When a beam of parallel alpha rays traverses matter, the several particles meet different experiences in passing through the atoms encountered. As a result of any cross-section of the beam there exist particles having quite different velocities, though Geiger has shown that at the start the alpha particles from radioactive material do not vary in velocity by as much as ½ per cent. Moreover, at the cross-section considered the ranges of the particles are different, that is, the distances the particles will proceed before they cease to be observable. "The alpha particles may be said to be straggled out, and hence the term straggling has been applied to this phenomenon by Darwin."

The Rutherford atom with its positively charged nucleus and its negatively charged satellite electrons lends itself to the calculation of the amount of straggling and accordingly theoretical computations have been made. On the other hand there are two experimental methods of measuring the same quantity. The first is somewhat indirect and depends on the ionization caused by the alpha rays at different sections of their path. The second is based upon direct counts of the number of particles at different parts of their path, and it is of necessity a laborious process since many particles must be counted.

The two results obtained from the experimental methods agree none too well, differing as they do by 50 per cent. or less, yet they do agree in furnishing values three or four times as great as those deduced by theory. "Furthermore the calculated straggling increases steadily with increase of range, while that observed is constant within the limit of error." This constancy the author interprets thus: "This can only mean that the excess straggling takes place only in the last two or three centimetres of the range. From experiments with gold foils which will be discussed later, it appears probable that the straggling is confined to the last few millimetres of the range." A group of gold leaves was located at different parts of the beam. It was found to cause more straggling near the end of the range than elsewhere. The significant feature in this investigation is that experiment brings to light certain features of straggling that the present theory is incompetent to explain. It is at the end of the range that the new effects are noted and it is just there that Shimizu, working on the paths of alpha particles made visible by cloud condensation, encountered still another departure from the behavior predicted by theory. "It is noteworthy that this anomalous behavior of the alpha particle occurs at low velocities, where practically no investigation of the scattering alpha particles has been carried out on account of the experimental difficulties of dealing with slow alpha particles." It may be well to keep in mind that the Rutherford atom was devised to account for a certain effect inexplicable by the views of atomic structure current at that time. If, after mature proving both of the experimental processes and of the theoretical deductions, they persist in remaining in contradiction, then our conception of the atom must be modified. G. F. S.

AN EXTRACTION APPARATUS WITH EXTRACT-RECOVERY AND SOLVENT-REGENERATIVE DEVICES.*

BY

LEWIS C. KARRICK,

Associate Oil-shale Technologist, U. S. Bureau of Mines,

AND

DOUGLAS GOULD,

Fellow, Metallurgical Research Department, University of Utah.

THE more common laboratory extraction methods are not entirely suitable for the treatment of certain finely divided substances, largely because of the fact that the fine particles clog the filter medium during the downward flow of the solvent. The apparatus, described and illustrated, was designed particularly with a view to the elimination of filter clogging troubles, by providing a space above the layer of pulverized material as a means of settling the suspended particles before they reach the filter. It was also desired to prevent compacting of the material under treatment, and this has been accomplished by employing an upward flow of the solvent. The new device has been found to operate very successfully in the extraction of soluble matter from pulverized substances.

The drawing illustrates the essential parts of the apparatus, and the course which the solvent takes in passing through the system is indicated by arrows. The solvent enters the bottom of the extraction tube and passes up through the sample being extracted, then out of the tube by way of the settling space and filter. It then flows into the extract-recovery flask, in which it is vaporized. The vapors pass to the reflux condenser, and from there the condensed solvent returns to the extraction tube.

The extraction tube may be made of glass or iron, otherwise the entire apparatus is of glass. A two-inch iron pipe has been used as an extraction chamber and has been found to be satisfactory. In the bottom of the tube is placed a mat which may be made of a layer of glass wool covered with a piece of cloth. This is used merely to provide a support for the material to be treated and to

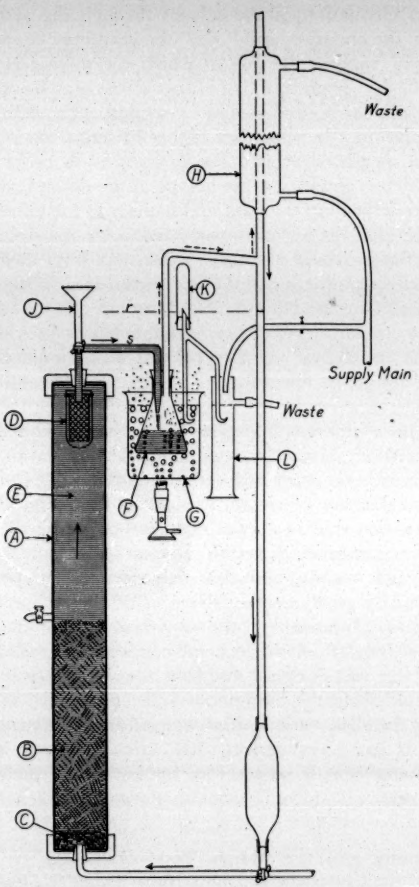
* Communicated by the Director of the Bureau of Mines.

aid in the uniform distribution of the solvent throughout the sample. A suitable filter is easily provided by using a Watman extraction thimble and fastening it around a one-hole cork-stopper through which is inserted a glass tube. The glass tube passes also through a cork-stopper in the upper cap of the extraction tube, thus providing a tight joint and allowing the filter to remain inside the extraction tube in contact with the solvent. Glass beads or a wire-gauze form should be placed inside the thimble to prevent collapsing of the filter. The solution, therefore, passes into the filter in a direction opposite to that usually employed, and then passes out through the glass-tube connection.

If, as a result of too rapid circulation of the solvent, the filter should begin to clog, the filter-cake may be released by temporarily reversing the flow of the solvent through the filter. To do this fresh solvent is introduced through the funnel (*J*), while the cock below the funnel is turned so that the new solvent will flow into the filter and not into the side tube leading to the extract-recovery flask. The solvent in the return-pipe leading down from the condenser must first be drawn off by means of the drain-cock provided. Then with the drain-cock again turned to the position shown in the drawing the solvent will flow back out of the extraction tube and rise up in the pipe below the condenser, as the fresh solvent is simultaneously added through the filter and funnel. The filter will clog very seldom and, except in rare cases, it will not be necessary to clean it during an extraction test.

Obviously the entire system should be filled with solvent throughout the run and there should be sufficient solvent in the recovery flask at all times to keep the extract in perfect solution. Should it be desirable to remove the collected extract and replace the flask with a new one during the test, this can be accomplished readily without the loss of solvent. The drain-cock at the bottom of the condenser-tube must be turned so that the solvent contained in this tube, as well as the solvent in the flask, will be permitted to pass out of the system and collect in the new flask. When the extract in the first flask is practically free from solvent, the new flask containing the recovered solvent may be substituted in its place, and extraction resumed. This procedure will be found convenient as the end of the test approaches, since it will show by the amount of extract recovered in the flask how near to completion the extraction has progressed.

The rate of extraction may be varied at will. Since the



Extraction Apparatus with Recovery and Regenerative Devices.

A. Leaching tube.
B. Pulverized sample.
C. Fibre mat.
D. Filter.
E. Settling space.
F. Extract recovery flask.
G. Boiler.
H. Solvent-vapor condenser.
J. Filter-washing and solvent-charging funnel.
K. Siphon.
L. Constant-level device.

velocity of circulation of the solvent through the system is dependent on the pressure-head "*r-s*," the head may be increased or decreased by varying the rate at which the solvent is vaporized from the flask. Therefore, the burner flame may be manipulated to bring about the desired rate of extraction. The bath (*G*) containing water, or other liquid of higher boiling point than that of the solvent, is placed around the flask so as to provide heating surface which is ample to cause boiling at the desired rate without danger of overheating the flask and damaging the extract in it.

In order that the apparatus may run continuously for several days at a time without attention, a constant-level device is provided which keeps the liquid (water in the case illustrated) at a definite height in the bath. *K* is a siphon and is an essential part of the constant-level device. The siphon is provided with a reservoir at its highest point to prevent an accumulation of air from interrupting its operation. This assures the continuous and uniform operation of the extraction apparatus.

When the extraction is finished the extract accumulated in the flask is freed of solvent by continuing the distillation until the excess solvent is removed and withdrawn from the system at the drain-cock below the condenser. Most of the solvent remaining in the extraction tube is drawn off at the cock placed in the side of the extraction tube. A certain amount of solvent will remain in the treated sample, and this may be entirely removed by distillation. By gently heating the sides of the tube with a flame (other means, if desirable), the vaporized solvent may be conducted out through the same cock and condensed by suitable means.

The device was designed and built for use in extracting from pulverized oil-shale the bituminous substance which is produced by heating the shale to its initial temperature of thermal decomposition. It has given perfect satisfaction and it is hoped that it will be found equally satisfactory for testing oil sands, leaching salt-laden earths, and for lixiviation purposes in general.

Germanium and the Marsh Test.—According to JOHN H. MÜLLER, of the University of Pennsylvania (*Catalyst*, 1922, vii, No. 7, 7), germanium hydride may be formed in the Marsh apparatus. Heat decomposes germanium hydride and causes the deposition of a reddish-brown metallic mirror, which might readily be mistaken for arsenic, since the common solvents for arsenic exert a similar action upon the mirror of germanium. J. S. H.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

EFFECT OF TEMPERATURE, DEFORMATION AND RATE OF LOADING ON THE TENSILE PROPERTIES OF LOW-CARBON STEEL BELOW THE THERMAL CRITICAL RANGE.[1]

By H. J. French.

[ABSTRACT.]

AN apparatus for determining tensile properties of metals at high temperatures (including limit of proportionality) is described in detail. Included also are the results of tensile tests at temperatures from 20° to 465° C. of various grades of half-inch boiler plate including the following:

(1) A.S.T.M. firebox steel;

(2) Marine boiler steel;

(3) Railway firebox steel.

A section of the report is largely devoted to a discussion of the effects of different amounts of rolling at room temperature and at blue heat (300° C.) on the properties of such steels throughout the range given, and data are presented to show the effects of partial annealing, particularly at temperatures near the blue-heat range, on the cold and blue-rolled metal.

A series of experiments is described to show some effects of tensional elastic overstrain on the proportional limit, tensile strength, and ductility of low-carbon steel at different temperatures, together with the subsequent behavior of the steel in both tension and compression upon ageing.

A modified form of the original apparatus is described whereby several rapidly moving dials indicating both stress and strain are simultaneously and repeatedly photographed by a motion picture camera, when rapid rates of loading are used.

Included also are results of tests showing the effects of both rapid and slow loading on the tensile properties of boiler plate at various temperatures.

In the general summary is given a brief discussion of the observed effects in the light of the amorphous metal theory, and to illustrate typical fractures photomicrographs are included.

* Communicated by the Director.

[1] Technologic Paper No. 219.

ELIMINATION OF WASTE—PAVING BRICKS.[2]

IN accordance with the unanimous action of the joint conference of representatives of manufacturers, distributors, and users, the United States Department of Commerce, through the Bureau of Standards, recommends that recognized types and sizes of paving brick be reduced to the following list:

Standard Sizes and Varieties.

Standard Sizes.

Width	Depth	Length	Width	Depth	Length
Inches	Inches	Inches	Inches	Inches	Inches
3	4	8½	3½	3½	8½
3½	4	8½	3½	3	8½

Standard Varieties.

Plain Wire-cut Brick (vertical fibre lugless)			Repressed Lug Brick		
3	4	8½	3½	3½	8½
3½	4	8½	3½	4	8½
Vertical Fibre Lug Brick			Wire-cut Lug Brick (Dunn)		
4	3	8½	3½	3	8½
4	3½	8½	3½	3½	8½
...	...	...	3½	4	8½
Hillside Lug Brick (Dunn)			Hillside Lug Brick (repressed)		
3½	4	8½	3½	4	8½

Specific Example of the Application of the Principle of Simplification to the Paving-brick Industry.—This recommendation describes the need for eliminating economic waste caused by the excessive variety in types and sizes of paving bricks, and shows the procedure used in reducing existing varieties from 66 to 7.

The industry initiated the action through its trade association, and the Government, through the Department of Commerce, endorses and publishes as its own those simplifications recommended by joint conferences of producers, distributors and users of the commodity.

These Simplified Practice Recommendations when accepted by the entire industry serve as commercial standards of practice with consequent benefit through decreased stocks, costs, and investments, and increased sales, turnover and income.

[2] Simplified Practice Recommendation No. 1.

NOTES FROM THE LABORATORY OF APPLIED SCIENCE, NELA RESEARCH LABORATORIES.*

IMPROVEMENTS IN PHOTOMETRIC EQUIPMENT FOR INTEGRATING SPHERES.

By A. H. Taylor, Physicist.

PHOTOMETRIC equipment in use with integrating spheres has not undergone any radical changes since the sphere was first introduced by Ulbricht. It usually consists of a bar photometer and accessories, including a set of standardized sectored disks and a Lummer-Brodhun photometer-head. In 1917, R. Von Voss,[1] in Germany, described a new type of photometer for use with spheres, but this does not appear to have come into use in this country. This laboratory has recently built apparatus designed along somewhat similar lines, but with several improvements which add to its convenience and usefulness.

The bar photometer used with the sphere usually has a candlepower scale attached to the comparison-lamp carriage, to read directly the candlepower of the lamp being photometered. In order to make this scale read correctly it is necessary to adjust the intensity of the comparison lamp by varying its voltage. This usually results in a color-difference between the lights compared. Another factor contributing to the color difference is selective absorption by the sphere paint. To overcome these color-differences it is necessary to prepare special color-filters, which is very difficult for most laboratories.

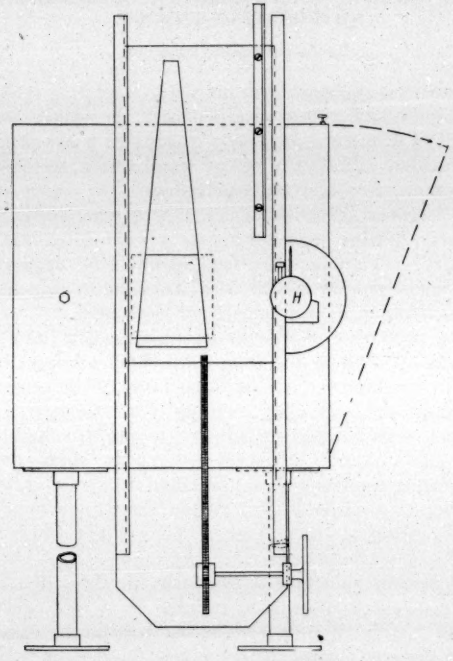
The apparatus built here is shown in the three illustrations. A suitable comparison lamp is enclosed in a rectangular box painted inside with the same paint as that used in the sphere. In the end of the box toward the photometer-head is an opal glass window, 8 cms. square, before which moves vertically a metal slide with a V-shaped opening. This slide carries a plate with three photometric scales, *viz.*, 25 to 75, 50 to 150, and 100 to 300 candles. Inside of the box at the top and bottom of the window are two horizontal broad bars (Fig. 3), the space between them

* Communicated by the Director.

[1] E. T. Z., **38**, p. 188, 605, 1917.

being adjustable by handwheel *H*. Hence the vertical width of the luminous window is adjustable by means of the horizontal bars and the average horizontal width by means of the movable *V*. The area of the window is directly proportional to the distance

FIG. 1.

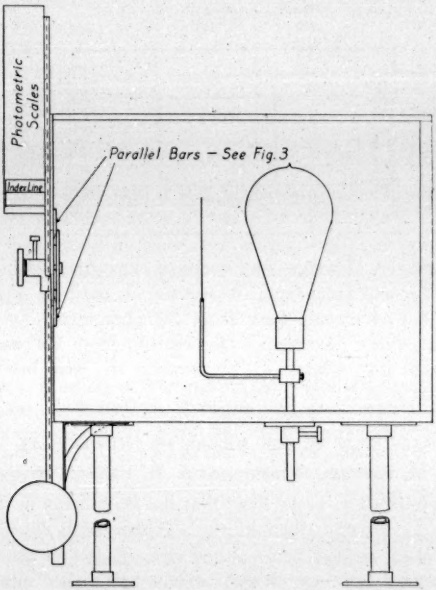


from the apex of the *V* to the point midway between the horizontal bars. This window is placed about 30 cms. from the photometer screen and illuminates it directly.

The sphere window, of a type originated by the Engineering Department several years ago, has two rough-ground flashed opal glass disks at opposite ends of a brass tube 4.5 cms. in diameter and white inside. The first disk is flush with the inner wall of

the sphere, and the second disk is imaged in the photometer tube. Just behind the first disk is placed a removable, thin metal plate with circular opening. It is possible to pass from one photometric scale to another by inserting a metal disk with the proper size of opening.

FIG. 2.



Door removed.

In operation a perfect color-match may be obtained between the two lights compared without the use of any color-filters. The photometric scales are made to read correctly by means of the adjustable horizontal bars shown in Fig. 3.

As compared with any type of bar photometer this photometric equipment has the following advantages:

1. It is less expensive to build and install.
2. It requires much less floor space.

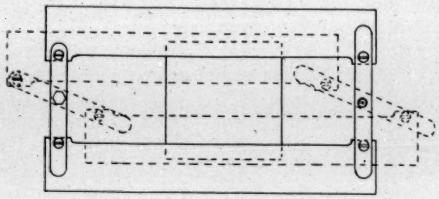
3. The photometric scales are uniformly divided, and for the highest precision a vernier may be used.

4. A perfect color-match may be obtained by the method described above.

5. The necessity for sectored disks is eliminated.

Tests made with this apparatus have proved it to be very

FIG. 3.



satisfactory. A further improvement has been achieved by omitting the opal glass from the window in the box, and placing the lamp out of line of view from the photometer, so that the photometer screen receives its illumination from the wall of the box opposite the opening. This method has also been proven satisfactory by trial.

MAINTENANCE OF GLASS AREAS IN INDUSTRIAL PLANTS.

By M. Luckiesh, Director, and A. H. Taylor, Physicist.

IT IS apparent on every hand that the glass areas in industrial plants are not usually systematically and adequately cleaned. The various ribbed, rippled, pebbled, and clear glasses in use transmit from 70 to 90 per cent. of the incident light when clean. The accumulation of soot, dirt, rust, etc., results in a very great decrease in transmission factor in a comparatively short period of time.

The table shows the results obtained with seven glasses just as they were taken from industrial plants. It is seen that cleaning resulted in an increase in transmission factor of from four to fifteen times. This means that the daylight illumination intensity in these plants would be increased from four to fifteen times if the entire glass were cleaned. In other words, if the illumination

intensity were only five foot-candles before cleaning it would be 75 foot-candles after cleaning glass No. 7. One of the glasses,

No.	Type of Glass.	Transmission.		Final Illumination Intensities in Terms of Initial Intensity.
		Before Cleaning.	After Cleaning.	
		Per cent.	Per cent.	
1	Plain clear	12	88	7.3 times
2	Plain clear	16	88	5.5 times
3	Fine ribbed	14	80	5.7 times
4	Fine ribbed	17	76	4.5 times
5	Fine ribbed	0.3	75	250.0 times
6	Wavy wire glass	13	80	6.1 times
7	Wavy wire glass	5	75.	15.0 times

No. 5, was so dirty that it was nearly opaque. Cleaning resulted in an increase in transmission factor of 250 times.

The investment in glass areas in industrial plants is considerable,[2] but the dividends from this investment are greatly reduced if the glass is not systematically and adequately cleaned.

A New Method of Measuring Corrosion Under Water. Investigation of Effect of Velocity. F. N. SPELLER and V. V. KENDALL.—Subaqueous corrosion is nearly proportionate to the concentration of oxygen dissolved in water, which fact is used for measuring the amount of corrosion in the experiments described. Water is passed through a certain length of ¼-inch, ½-inch, and ¾-inch commercial steel pipe uncoated, and the corrosion is measured by the difference in concentration of dissolved oxygen. Time of contact was held constant by varying the length of pipe. Velocities from 1/10 foot per second to 8 feet per second were obtained. Corrosion-velocity curves are given for each size pipe, for temperatures ranging from 60° to 170° F. Corrosion is found to increase with velocity in all cases, but at a decreasing rate. Rate of corrosion accelerates rapidly with rise in temperature over 90°, velocity and all other conditions being constant. This method of measuring corrosion is applicable to the investigation of the influence of other factors on subaqueous corrosion, such as composition of the metal, character of the water, etc. (A. C. S. Abstract Service.)

[2] "Cost of Daylight," M. Luckiesh and L. L. Holladay, Abs. JOUR. FRANK. INST., **194**, 1922, p. 252; *Trans. Illum. Eng. Soc.*, 1922.

Resumption of Exchange Professorship.—The Karl Schurz Memorial Professorship in the University of Wisconsin was founded in 1910, for exchange professorships with the German universities. The exchange was interrupted by the war, but will be resumed in the coming academic year by lectures by Professor A. Sommerfeld, who holds the chair of Mathematical Physics in the University of Munich. Two courses will be given, one on Atomic Structure and the second either on the Analysis of Wave Propagation or on the General Theory of Relativity. The graduate school of the University also announces that Professor Svedberg of the University of Upsala will be present during the latter half of the academic year and will lecture and conduct seminars in the field of colloid chemistry. H. L.

The Removal of Small Amounts of Carbon Monoxide from Gas Streams by Passing Over Heated Granular Soda Lime. ROBERT E. WILSON.—The problem of the complete removal of CO from gas streams is of importance in a number of industrial applications. One or two German patents have mentioned the use of granular soda lime at fairly high temperatures for the purpose, but they offer no quantitative data. This paper describes a series of experiments at temperatures varying from 250° to 550° C. and using soda limes of varying composition. The results show that high alkali soda limes give complete removal at the lowest temperature (around 350° C.), providing water vapor was present and hydrogen absent. In the presence of considerable amounts of hydrogen, removal is not complete under any conditions tried. The fundamental reaction involved is apparently:

$$CO + H_2O + NaOH - Na_2CO_3 + H_2$$

(A. C. S. Abstract Service.)

Diffusion in Deformed Gels.—EMIL HATSCHEK (*Science Progress*, 1922, xvii, 86–94) has studied the diffusion of aqueous solutions of salts into deformed gels of gelatin. In one series of experiments, the gel contained lead acetate; when potassium chromate solution diffused into this gel, lead chromate (chrome yellow) was deposited in zones. In another series of experiments, the gel contained trisodium phosphate; when the solution of a calcium salt diffused into this gel, tricalcium phosphate was precipitated in zones. The shape and arrangement of these zones showed that it is highly improbable that the diffusion velocity varies with the varying degree of compression. Apparently the gel remains isotropic for diffusion under stress; and the velocity of diffusion is the same in a deformed gel as in an unstressed gel. J. S. H.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

SOME NEW SENSITIZERS FOR THE DEEP RED.[1]

By C. E. K. Mees and G. Gutekunst.

THREE dyes have been selected as having interesting properties from a number investigated. The first of these is naphthacyanole, prepared by the condensation of betanaphthaquinaldine ethiodide with quinoline ethiodide in the presence of formaldehyde in alcoholic potash, the dye being a homologue of pinacyanol. It sensitizes with a strong maximum in the deep red at 690$\mu\mu$ and a minimum in the green.

Acetaminocyanole was prepared by the condensation of 6-acetaminoquinaldine ethiodide with quinoline ethiodide in the presence of sodium ethylate and formaldehyde. This gave a maximum at 730$\mu\mu$. It was unstable in the presence of small amounts of water and is not thought to be generally useful.

Kryptocyanine was prepared by the condensation of lepidine ethiodide as described by Adams and Haller. In normal concentrations it gives severe fog, but in dilute concentrations good results are obtained, the maximum being at 760$\mu\mu$. It is thus the most powerful sensitizer for the near infra-red known and is expected to have applications in astronomical photography. In the extreme infra-red, it is inferior to dicyanine.

Titrations.—J. L. LIZIUS and NORMAN EVERS (*Analyst*, 1922, xlvii, 331–341) have studied the titration of acids and alkalies. They recommend the use of "mixed indicators" for certain titrations. Thus phenol-violet, a mixture of 1 part of phenolphthalein and 6 parts of thymol blue, is used for the titration of weak acids; it gives a blue color at the neutral point and a violet color with alkalies. The results obtained by titration are increased in accuracy when the titrations are carried to a definite shade of color instead of to the change of color of the indicator. Observance of this procedure renders possible titrations which are otherwise impracticable.

J. S. H.

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* Communicated by the Director.

[1] Communication No. 147 from the Research Laboratory, Eastman Kodak Company and published in *Brit. Jour. Phot.*, 1922, p. 474.

Cod-liver Oil.—J. C. DRUMMOND and S. S. ZILVA have made a study of the Norwegian cod-liver oil industry under the auspices of University College and the Lister Institute, London (*Jour. Soc. Chem. Ind.*, 1922, xli, Transactions, 280–284). Extraction of the oil from the livers by the old rotting process is rarely practiced. However, the inactivation of the fat-soluble vitamine during the rotting is not as serious as might be expected. The oil is usually extracted by treatment of the livers with direct steam or in a steam-jacketed pan. From the viewpoint of preservation of the vitamine, the steam-jacketed pan is possibly slightly superior to direct steam. One of the chief aims of the more progressive manufacturers is to avoid oxidation of the oil. Posetran is a second fraction obtained in the extraction of the oil; it passes drop by drop through filter bags, yet does not suffer any appreciable loss of the vitamine. In the process of refining, the oil is cooled to a temperature of 0° to –10° C. in order to remove the stearine. At times, the oil may also be treated with an adsorbent, then passed through a filter press. This treatment removes pigments. The process of removing the stearine has an almost negligible result on the vitamine content of the oil. The stearine is the equal of butter, if not superior to that food, as a source of the fat-soluble vitamine. Therefore the stearine should be used as a food, although it is now applied for technical purposes. The modern white cod-liver oils are as valuable as the dark oils from the viewpoints of nutrition and medicinal value. J. S. H.

A New Form of Precision Hydrometer. C. W. FOULK.—This hydrometer consists of a glass float moving freely in a glass tube carrying a suitable scale. Between the float and the lower end of the tube a light chain hangs in a catenary curve. The float is ballasted so as to be in approximately submerged floating equilibrium in the liquid to be tested. The final adjustment to exact equilibrium is automatically made by the action of the chain, and this position of the float is then read on the scale. With a properly calibrated instrument density determinations accurate to one unit in the fourth decimal place can be made in a couple minutes. (A. C. S. Abstract Service.)

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

ANALYSIS OF CRUDE VEGETABLE OILS.[1]

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE object of the existing methods for testing crude oils is to determine the quantity of refined oil that can be obtained from a crude oil when the refining is conducted in a particular way which simulates the commercial refining process. Some new methods have been developed by which it is possible to determine, among other things, the absolute quantity of neutral oil present. When a crude vegetable oil, dissolved in petroleum ether, is shaken with an aqueous potassium hydroxide solution, the free fatty acids are neutralized, the coloring matter is precipitated, and certain compounds of fatty acids other than glycerides are decomposed. Adding 50 per cent. alcohol causes the mixture to separate into two layers—a petroleum-ether solution of neutral oil and an alcohol-alkali layer containing the saponified fatty acids, coloring matter and other impurities. The two layers may be separated, the petroleum ether distilled from the ethereal solution and the neutral oil weighed.

It is possible to determine the quantity of fatty acids in the alcohol-alkali solution and also the quantity of alkali absorbed by the crude oil. Fatty acid glycerides are not decomposed by the method. A recovery of 100 per cent. of mineral oil was obtained by applying the method to dry neutral refined oil. Detailed directions for making this determination on cotton-seed, peanut, and soya bean oils have been prepared.

DEVELOPMENT OF PARATYPHOID-ENTERITIDIS GROUP IN VARIOUS FOODSTUFFS.[2]

By Stewart A. Koser.

[ABSTRACT.]

AN investigation was conducted to gain some idea of the ability of several type strains of the paratyphoid-enteritidis group to develop in miscellaneous foodstuffs, such as various vegetables, fruits, meats, and evaporated milk. The effects of different

* Communicated by the Chief of the Bureau.

[1] Published in *Cotton Oil Press*, **6** (August, 1922): 33.

[2] Published in *J. Infect. Dis.*, **31** (1922): 79.

conditions, such as temperature of incubation, the hydrogen-ion concentration and the texture of the food, were considered in relation to multiplication and the ability to spread throughout the foodstuff.

All the strains of the Gaertner group multiplied readily in the liquor of several common cooked vegetables, with the exception of the highly acid sauer kraut. In the fruit juices a rapid destruction of the organisms occurred. In several meat products Gaertner group organisms exhibited a marked ability to spread from one original point of inoculation throughout the foodstuff, although this occurred only under optimum temperature conditions.

The development of the Gaertner group in foodstuffs is usually not accompanied by visible alteration or spoilage. The present observations on this point are in accord with the reports of previous outbreaks of "food poisoning" caused by this group of organisms.

BY-PRODUCTS FROM CRUSHING PEANUTS.[1]

By J. B. Reed.

[ABSTRACT.]

CRUSHING whole peanuts by the expeller process usually gives a meal containing from 34.4 to 38.6 per cent. of protein. Crushing peanuts from which the hulls have first been removed by the hydraulic process gives a meal containing from 45.3 to 49 per cent. of protein.

Peanut meal is an excellent feed. Peanut hulls, however, have a low feeding value and can not be economically shipped any great distance for use as a feed.

It is possible to determine approximately the percentage of hulls in a mixture of peanut meal and hulls, either from the fibre content or from the protein content. It is probable, however, that the figures obtained from the fibre content will be more nearly accurate.

The composition of peanut skins removed by hand differs from that of peanut skins obtained from the peanut-butter plants. The composition of peanut germs is similar to that of the meats, with somewhat lower oil and somewhat higher ash contents.

A sample of meats from the Spanish variety of peanuts was found to contain 5 per cent. of sugars and 4.7 per cent. of starch.

[1] Issued as U. S. Dept. Agr. Bul. 1906, August 12, 1922.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, September 6, 1922.)

HALL OF THE INSTITUTE,
PHILADELPHIA, September 6, 1922.

DR. JAMES BARNES *in the Chair.*

The following report was presented for final action:

No. 2767: Audion. The Elliott Cresson Medal to Dr. Lee de Forest, of New York.

The following report was presented for first reading:

No. 2796: Noiseless Typewriter.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, September 13, 1922.)

RESIDENT MEMBERS.

MR. ROLAND L. EATON, 20 South Eighteenth Street, Philadelphia, Pennsylvania.

PROF. ERNEST EDWARD JOHNSON, Professor of Physics, Northeast High School, 2101 W. Ontario Street, Philadelphia, Pennsylvania.

NON-RESIDENT.

MR. ROBERT HATFIELD IRONS, President, Central Iron and Steel Company, Harrisburg, Pennsylvania.

MR. JOHN E. SYMONS, Mechanical Engineer, The Texas Company, 17 Battery Place, New York City, New York.

CHANGES OF ADDRESS.

MISS CAROLINE D. BLACKBURN, 7028 Paschall Avenue, Philadelphia, Pennsylvania.

MR. K. BRADDOCK-ROGERS, Trinity College, Hartford, Connecticut.

MR. H. CALVERT, President, Baird-Osterhout Company, 2114 Sansom Street, Philadelphia, Pennsylvania.

MR. EDWIN FRANK, 1015 Shepard Avenue, Milwaukee, Wisconsin.

PROF. ARTHUR M. GREENE, JR., Princeton University, Princeton, New Jersey.

DR. A. E. KENNELLY, Harvard University, Cambridge, Massachusetts.

MR. T. A. LAWES, 9794 Newton Avenue, Cleveland, Ohio.

MR. RALPH H. MULLER, 485 Rogers Avenue, Brooklyn, New York.

PROF. I. M. RAPP, The University of Montana, Missoula, Montana.

MR. C. E. SARGENT, P. O. Box 99, Clinton, Iowa.

MR. S. WEINBERG, Sunderland House, 35th Street and Powelton Avenue, Philadelphia, Pennsylvania.

MR. JAMES A. WRIGHT, Wright-Fisher Engineering Company, 600 McGill Building, Montreal, P. Q., Canada.

NECROLOGY.

EXCERPT FROM THE MINUTES OF A MEETING OF THE BOARD OF MANAGERS HELD SEPTEMBER 6, 1922, RELATIVE TO THE DEATH OF MR. COLEMAN SELLERS, JR.

Mr. Howson, in referring to the great loss which the Institute and the community have sustained in the death of Mr. Coleman Sellers, Jr., said that Mr. Sellers' service to the Institute and through the Institute to the Engineering profession could not be measured.

Becoming a Member of the Institute in 1873, he served for twenty-seven consecutive years on the Committee on Science and the Arts. In 1906, he became a member of the Board of Managers, in 1912 he was elected Vice-President, and in 1917 he was appointed Chairman of the Institute's Committee on Endowment.

On motion, duly seconded, the following preambles and resolutions were unanimously adopted:

Whereas, in the death of Mr. Coleman Sellers, Jr., Vice-President, the Institute has lost one of its best friends and strongest supporters,

Whereas, a deep sense of personal loss is felt by every member of the Board in the death of a friend, whose qualities both of heart and mind endeared him to all, therefore, be it

Resolved, That the Board of Managers of The Franklin Institute records with deep sorrow the death of its esteemed and distinguished Vice-President, Mr. Coleman Sellers, Jr., whose activities have been of inestimable value to the Institute and to the community.

Resolved Further, That a copy of the above preambles and resolution be forwarded to Mrs. Sellers.

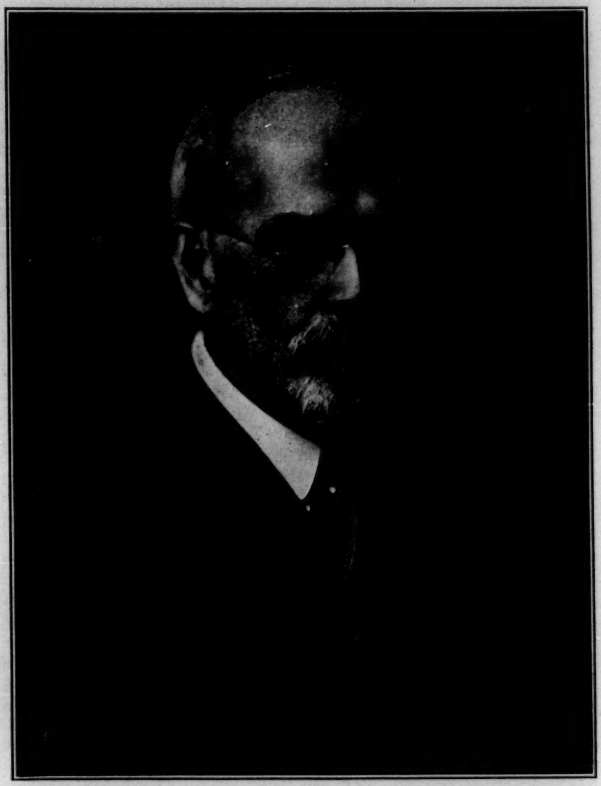
Resolved Further, That the above preambles and resolutions, together with the following biographical sketch of Mr. Sellers, be published in the JOURNAL.

Coleman Sellers, Junior, was born at Cincinnati, Ohio, September 5, 1852, the eldest son of Coleman Sellers and Cornelia, daughter of Horace Wells, a native of Connecticut, who with his father, Oliver Wells, established the Cincinnati Type Foundry.

In his paternal line he was of the sixth generation of progenitors engaged consecutively in the mechanical arts and who had contributed by useful inventions to their advancement. His father was the eldest son of Coleman Sellers, of Philadelphia, a mechanical engineer, whose firm built some of the early locomotives used in Pennsylvania and is credited with basic improvements in their design that have survived in their present construction. His wife was Sophronisba Peale, daughter of Charles Wilson Peale, the portrait painter of the Revolutionary period.

At the time of Coleman Sellers, Jr.'s, birth, his father was Superintendent of the Niles Locomotive Works of Cincinnati and a few years later in 1856 returned to Philadelphia as chief engineer and designer in the machine works of William Sellers and Company.

Coleman Sellers, Jr., was educated in private schools in Philadelphia and



COLEMAN SELLERS, JR.

entered the University of Pennsylvania in the Sophomore year, Class of 1873, and throughout his course was a First Honor man in his standing as a student. In University activities he held a prominent place, was Moderator of the Philomathian Society, Class President, Class Prophet, and finally Valedictorian at graduation when he received the degree of Bachelor of Science. In 1876 he received the degree of Master of Science after shop tests and thesis relating to steam boiler injectors.

Upon leaving college in 1873 he entered the works of William Sellers and Company under instruction to learn the trade and after experience as a journeyman machinist, he became foreman of a department, and in due time was transferred to the draughting room over which he was subsequently placed in charge.

Upon the incorporation of the firm he was appointed assistant manager and held that position from 1886 until 1902 when he was appointed Engineer; his father, Coleman Sellers, having previously retired from the business.

After the death of William Sellers, Coleman Sellers, Jr., succeeded him as President and Engineer and continued in that capacity until his death.

Although Coleman Sellers, Jr., is not credited with the inventions, such as marked the career of his father, his sound judgment, ingenuity and experience contributed in full measure to maintaining the high reputation of his Company as designer of machine tools and appliances in its special field.

While he did not seek public activities outside of his business, he accepted such duties as occasion offered both for the advancement of his profession and as a public-spirited citizen. He was one of the founders of the Engineers Club of Philadelphia and for fifty years active in The Franklin Institute lecturing on subjects in which he had special knowledge and serving on its various committees and for many years as one of its Board of Managers and as Vice-President.

From 1909 until 1913 he was President of the Chamber of Commerce of Philadelphia, and from 1908 until his death, one of the three State Commissioners of Navigation for the Delaware River and tributaries, taking particular interest in the training school for seamen conducted under its auspices.

In politics he was a Republican of independent principles and generally allied with reform movements without regard to party.

He was a member of the American Philosophical Society, the American Society of Mechanical Engineers, American Society of Naval Architects and Marine Engineers, American Academy of The Fine Arts, the University Club of Philadelphia, the City Club, Contemporary Club, Pennsylvania Society Sons of the Revolution and the New England Society of Pennsylvania.

During the late war, he was tireless in the discharge of his duties as head of the draft board in his district and in consequence of his devotion to the task his health was impaired, and to this circumstance is attributed the condition that led to his last illness.

In 1881 Coleman Sellers married Helen Graham Jackson, of Brookline, and is survived by one son, Coleman Sellers, 3rd, and three daughters.

His death occurred after an acute illness of several months, August 15, 1922, at Bryn Mawr, Pennsylvania.

Mr. John C. Bullitt, 3rd, 1811 Walnut Street, Philadelphia, Pennsylvania.
Prof. Jefferson E. Kershner, 445 W. Chestnut Street, Lancaster, Pennsylvania.

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BOOK NOTICES.

Molecular Diffraction of Light. By C. V. Raman, Palit Professor of Physics in the Calcutta University. 103 pages, 8vo. Printed by Atulchandra Bhattacharyya at the Calcutta University Press, 1922.

This book, a product of scientific activity at the Calcutta University and dedicated to the Vice-Chancellor, Sir Asutosh Mookerjee, attests the generous response of the Asiatic mind to the stimulus of western physical thought. The recent pages of the *Philosophical Magazine* have borne ample witness to the value and diversity of this reaction.

Such a volume as this cannot but be welcomed wherever throughout the world there is interest in understanding the phenomena of light. The author presents as the subject of the book the important question "Does any departure from perfect regularity of the light-propagation arise from the discontinuous structure of the medium?" and holds so well to the course he has laid out for his discussion that the reader who has followed the nine short chapters with comprehension feels himself to have advanced through familiar ground up to the very frontiers of the subject and, in addition, to know in just what direction to look for extensions of territory. Would that more physicists found time and inclination to write reports on the present status of limited fields of investigation with which they are familiar and in which they have made important contributions!

In gases the accepted theory of molecular diffraction is that proposed by the late Lord Rayleigh for the explanation of the blue of the sky. "The individual molecules in a gas through which the primary waves of light pass are regarded as secondary sources of radiation, each molecule acting more or less as it would in the absence of its neighbors." The mathematical development of this principle by its proponent leads to a relation between the wave-length of the incident light, the index of refraction of the medium and the intensity of the diffracted light that in the main explains in a satisfactory manner a large body of observed phenomena. The author examines the correctness of certain assumptions made in the derivation of this relation and concludes that their validity rests on (1) "the conditions being such that the compressibility of the medium is given with sufficient accuracy by Boyle's Law" and on (2) "the complete non-uniformity in the spatial distribution of the molecules in so far as very small volume elements are concerned."

In the second chapter are presented experimental results of the study of the scattering of light by gases. There is a marked difference between the polarization of the scattered light as predicted from the Rayleigh theory and as actually observed. Rayleigh accounts for this by assuming that the molecules possess three axes of symmetry and are oriented at random. Others have sought an explanation by using the Bohr-Sommerfeld model of the molecule but with little success.

When we come to the chapter on "Atmospheric Scattering and Twilight Phenomena," it is interesting to note how many references relate to American work. Abbot and Fowle, Luckiesh in the Journal of The Franklin Institute, Kimball and W. J. Humphreys are among these cited. With the last named, the author is in positive disagreement on one point. Humphreys holds that the conditions of the sky at dawn and sunset are so complicated that a rigid analysis leading to an adequate explanation of the light effects then

occurring can scarcely be hoped for. Raman, on the other hand, states that twilight is due to the illumination of the dust-free upper portions of the atmosphere by sunlight which in its course has not traversed the dusty lower air, and claims that "We are entitled to regard the problem as one of practically simple molecular diffraction, and the complications arising from secondary scattering are far less important than might be imagined. Sufficient work has been done, however, to show that the problem of twilight, at least in its essential features, is capable of being subjected to numerical computation of intensities from theory for detailed comparison with the observations."

Lord Rayleigh as long ago as the end of last century emphasized the inapplicability of his theory of molecular scattering of light to the cases of liquids and solids. In the face of this some recent investigators have suggested that the theory mentioned may none the less be applied to liquids. The author combats the propriety of this, basing his objections on the failure of liquids to conform to Boyle's Law in their pressure-volume relations and further on their departure from the condition of complete non-uniformity of spatial distribution. The molecules of a liquid occupy in actuality a larger fraction of the volume of the containing vessel than do the molecules of a gas at ordinary pressure in the same vessel. In the former state, therefore, the molecules have less opportunity to depart from uniformity of distribution than in the latter. Since then the scattering of light by liquid molecules cannot be explained by Rayleigh's theory, recourse is had to the "theory of fluctuations" developed by Einstein and Smoluchowski, wherein the scattering of light is attributed not to the action of individual molecules, but to small local variations of density brought about by the heat agitation of the molecules. The formula for the intensity of scattered light derived from this theory is more general than that of Rayleigh. In fact, it reduces to the latter when certain relations characteristic of gases are introduced into it. An account is given of an attempt to compare values of intensity derived from the formula with observed values. In spite of the difficulty of getting a specimen of water free from motes, a satisfactory agreement was found. Yet this formula, which holds for such different conditions of matter as gas at ordinary pressure, gas near the critical point and a liquid, seems to cease to hold when the attempt is made to apply it to saturated vapors below the critical temperature. Careful experiments are greatly needed either to establish or to remove this discrepancy. Such experiments are now actually in progress.

The color of the sea is treated in a separate chapter and experiments of so interesting a character are described that it would seem a loss of opportunity for any physicist hereafter to take a voyage without a Nicol in his baggage. In the July, 1922, number of this JOURNAL, page 106, there is given some account of Raman's work on the color of sea water. He concludes that "The blue color of the scattered light is really due to diffraction, the selective absorption of the water only helping to make it a fuller hue."

The study of the scattering of light in crystals is in its incipiency. The effect has been observed in quartz, rock-salt and ice. Quantitative measurements are now being made in the Calcutta laboratory. Very little is known about the relations of amorphous solids to the scattering of light. Optical glass has a scattering power 300 times as great as that of pure air according to Rayleigh.

In the final chapter the relations of molecular diffraction to the quantum theory of light are discussed. "In the year 1905, Einstein put forward the hypothesis that the energy of a beam of light is not distributed continuously in space but that it consists of a finite number of localized indivisible energy-bundles or 'quanta,' capable of being absorbed or admitted only as wholes. The theory had some notable successes to its credit, especially the prediction of the photo-electric equation and the explanation of the phenomena of ionization of gases by X-rays. Nevertheless, it has been felt that very serious difficulties stand in the way of its acceptance." It is pointed out that this theory of Einstein lends itself well to an explanation of the experimentally found quantity of scattering in a highly compressed gas. Should it become established that the scattering mentioned is inconsistent quantitatively with the Einstein-Smoluchowski theory, then this, which is based on a continuous distribution of light energy through space, may need to be abandoned in favor of the quanta theory.

The book abounds in suggestions for fruitful experimentation. There is perspective in its treatment. One does not lose sight of the woods in looking at the trees. GEORGE F. STRADLING.

LIQUID FUEL AND ITS APPARATUS. By Wm. H. Booth, F.G.S., Member of the American Society of Civil Engineers. Second edition. 308 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, no date. Price, $4.00 net.

The subject of liquid fuel has been a prominent feature of journal literature for several years. There is, indeed, a prospect of serious international complications over it, in view of the fact that oil supplies are not uniformly distributed, and the great maritime nations are now aware of the probability of oil-burning plants being generally established for motive power in ships. Extensive application has already been made, some of the largest passenger ships having been converted into oil-burners, with great saving as to labor and storage, but a new trouble has arisen, in consequence of the fouling of harbors and streams by the escape or discharge of oil.

The present work is an enlarged edition of one issued about a dozen years ago. In this interval great advances have been made not only as to the importance of liquid fuels, but in the apparatus for their use. The author attributes to Mr. Holden of the Great Eastern Railway of England, the first successful employment of liquid fuel in that country. He used surplus tar at first, but the road is now using Texas oil. The railways in southern Russia have used petroleum residuum for many years. In the preparation of this second edition, the author has searched the standard literature, and has also used information from manufacturers of apparatus, when such statements have seemed trustworthy.

The first really practical and efficient employment of liquid fuel for steam-raising purposes seems to have been due to Thomas Urquhart, who used it by means of a spraying system in locomotives on the Grazi and Tsaritzin Railway of Russia. An account of this appeared in the proceedings of the British Institution of Mechanical Engineers in 1884. The early liquid fuels were tars or residua; the modern liquid is mostly crude oil. Mr. Booth considers that the method has passed the experimental stage, yet the possibility of exhaustion of petroleum supplies always hangs like the Damoclean sword over the world. There seems to be no reason to fear early exhaustion of coal, but labor problems

in coal mining are becoming more and more serious every day. The present production of mineral oil is a mere fraction of the coal production. Oil has a much higher calorific value than coal, being about 30 per cent. better, weight for weight, than the best coals. There is but one satisfactory way as yet known for burning liquid fuel, namely, by atomizing it.

This book gives a concise but clear and full account of the methods and apparatus employed in the use of liquid fuels and is a useful manual for motive power engineers. HENRY LEFFMANN.

THE CHEMISTRY AND TECHNOLOGY OF GELATIN AND GLUE. By Robert Herman Bogue, M.S., Ph.D., Mellon Institute Research Fellow and Research Chemist for Armour Institute. x-644 pages, 8vo. New York, The McGraw-Hill Book Company, 1922. Price $6.00 net.

Few substances employed in the industries are more familiar and have been longer in use than glue. In a purer form, termed "gelatin," it has found many applications wholly different from that for which it was originally employed. Notwithstanding the importance of these products, and the long time in which they have been known, the chemistry of them is still imperfectly known. The book in hand is a worthy effort to summarize the existing literature which is very extensive, but was not yet in book form. The existing text-books are not up-to-date. The subject is treated in this work mostly from the chemical point of view, and primarily for the student and research worker. Doctor Bogue gives us as an introduction, an interesting and and useful summary of the early history of the making and use of glue, which was prepared, as might be expected, first from the skins of animals. Here he unequivocally allies himself with those who regard man as an evolution from a lower order of animals. A granite carving, probably 4000 years old, found in Egypt, shows the working up of a tiger's skin and an allusion in the Iliad refers to the larding of an ox-hide for making it supple. Early allusions in Biblical and classic literatures are also noted. A frontispiece is a reproduction of an Egyptian carving of about 1300 B.C. showing the use of glue for veneering and joining. It is stated that the period is that of the Exodus, but there is an uncertainty about the date of that event. However, there is no reason to doubt that the carving is very ancient. The manufacture of glue in Europe was doubtless begun at an early period, but actual records seem not to go back of the last decade of the seventeenth century. The first mention in British patent literature is 1754. The substance was prepared from the tails and fins of whales and other fish refuse. Not long after a patent was taken out for the preparation of "isinglass," made from the internal membranous parts of fishes. The use of high-pressure boiling was introduced in 1822. An edible preparation was first the subject of a patent by Arney in 1846.

After these historical, etymological and statistical summaries, the chemistry and technology of the products are taken up. Over two hundred pages are devoted to the theoretical aspects. This section begins with a statement of the constitution of the proteins as a class, followed by a specific discussion of gelatin and its immediate allies. Large space is given to the physical chemistry of the gelatins, and then their characters as lyophilic and amphoteric colloids are discussed. Very extended and elaborate discussion is given to

the latter questions and those who are not familiar with the existing development of colloid chemistry will find many curious and astonishing facts.

The technologic part covers a little more than half the book. The manufacture of glue and gelatin is treated by Ralph C. Shuey, M.S., of the Redmanol Chemical Products Company. This section covers all phases of manufacture, including hide glue, bone glue, ossein and gelatin, the last term, being by common consent applied to the finer varieties, especially those employed as food. In this line great care is necessary. The whole plant must be constructed so that entire cleanliness may be secured. As the vessels must be sterile, wooden containers are unsuitable, and as the liquors are generally kept slightly acid, some of the common metals are inapplicable. Aluminum seems to be the best. One of the dangers is that arsenic may be applied to the raw material as a preservative, and thus be found in the finished product. Some years ago the United States Government established minimum limits for arsenic in commercial gelatins. Sulphites are often used for bleaching and may also remain. This impurity is equally a matter of official control. Some years ago LaWall and Leffmann showed that some of the highest priced gelatins in the market (importations from Europe) contained considerable amounts of sulphites. The most objectionable impurity, at least the most frequent, is bacterial contamination. Unfortunately, as the author of the section points out, contaminated and even slightly decomposed stock is not infrequently put on the market and is not always easy to detect. He recommends a rigid system of factory inspection.

Other sections of the second part are devoted to water-proof glue, marine glue, testing of samples, detection of glue and gelatin, and the uses and applications of all grades. The detection of gelatins and glues, as well as of some carbohydrate products of similiar properties (*e. g.*, agar) has become an important part of the work of the food chemists, and those engaged in food analysis will welcome the excellent account which is given of the methods applicable to foods and other articles.

The book is a most welcome addition to our literature on the subject. A good deal has been written on the more abstruse phases of colloid action, but the work before us is a comprehensive and valuable summary of the special subject. The mechanical execution is excellent, the literary style commendable and the more than one hundred illustrations, including diagrams and apparatus, serve to make clear the statements. Good indexes and a number of useful tables add still further to the value of the work.

HENRY LEFFMANN.

THE CHEMISTRY OF COMBUSTION. By J. Newton Friend, D.Sc., Ph.D., F.I.C. 100 pages, contents, bibliography, notes and index, 16mo. New York, D. Van Nostrand Company, 1922. Price $1.25 net.

This book, one of a series of monographs of which several have already appeared, is the outcome of a lecture course at the Technical School at Birmingham, England. The chemistry of combustion has been a storm-centre in chemical theory for a long while. The disputes in the eighteenth century concerning phlogiston constituted a prominent feature in the science of that period. The deeper feelings of chemists were aroused over the attack and defense of the views. It is said that Cavendish relinquished his activities in research when he found that chemists generally were about to

abandon the theory. Priestley was a stout defender of it. Doctor Friend's book is principally intended to set forth the present day views of the phenomena of combustion, hence discarded theories are given but little space. The subject of phlogiston receives but three pages, in which, however, a good summary is given of development of it. The term is due to Stahl. Reference is made to the Arabic writings of Geber in the eighth century, but it is doubtful whether the works thus ascribed are genuine. Bibliographical references enable the student to secure further details if desired. After this preliminary consideration, the author passes to the study of the chemistry of combustion under modern conditions and gives many data which are of great interest and value in the industries. At the present day when fuel problems are so complex and insistent, and when liquid and gaseous materials are steadily displacing the solids, all the physical and chemical questions concerning combustion are important. The nature of ordinary combustion was established in the latter part of the eighteenth century, although some faith in "phlogiston" lingered later, but many important points still remained incompletely observed until our own time.

The chapter on flame is an instance of the changing viewpoint. For many years, text-books have defined flame as "any volatile matter burning," but Doctor Friend defines it as a mass of gas raised to incandescence, and, therefore, recognizes flame without combustion, instancing a gas rendered luminous by electric discharge. The classic illustration of the candle flame is discussed at some length. Four zones are distinguished, and the long-received view that the luminosity is entirely due to incandescence of separated carbon is declared not wholly sufficient. Frankland, in 1867, showed experiments which threw doubt upon the common view (due to Davy) and ascribed the light to dense gases, but the question is not settled, and Doctor Friend thinks that the explanation of the phenomena of the candle may involve both views. We are not surprised that it is suggested that the luminous substance may be in the colloid condition. The book is well worth the attention of teachers and fuel engineers.

HENRY LEFFMANN.

STANDARD METHODS OF CHEMICAL ANALYSIS. Edited by Wilfred W. Scott, assisted by many collaborators. Third edition, thoroughly revised and greatly enlarged. Two volumes, 1567 pages, contents and index, 250 illustrations and 3 colored plates. New York, D. Van Nostrand Company, 1922. Price $10.00 net.

Thirty-six collaborators have taken part in the revision of this book, which has been so much increased in size as to necessitate presentation in two volumes. It covers a wide range of analytical work, and in consequence of the extensive share that specialists have had in its preparation gives to the chemist an up-to-date treatise. The preface enumerates many additions and extensions. The first volume is taken up with inorganic substances, giving special space to each important element; the second volume is devoted to important compounds and industrial products. Illustrations are freely used. The comparison plates of the spectrum by the prism and by the grating are very brilliant and well executed, but it is a question whether such illustrations are worth their cost. The worker who uses the instruments will obtain vivid pictures for himself, and will not be likely to rely on the plate, while to those who do not have the apparatus the plates can be of little value.

A work that has gone to the third edition within a little over five years, as shown by the date of the preface to the first edition, evidently has merit, and examination shows that it is comprehensive, clear and carefully written. The reviewer naturally turns to the chapter relating to the field in which he has especially worked, and in doing this is moved to wonder why, in describing the process for volatile acids in butter, the tedious alcohol saponification is given instead of the glycerol-soda method which is now generally used, being, indeed, the exclusive official method in several European countries. The mechanical execution of the book is good. The numerous illustrations have compelled the use of a very smooth shining paper that is not quite as agreeable to the eyes as the papers commonly used in scientific works.

In the space available for a review it is not possible to point out in detail the merits of the book or to advise as to material improvements if such advice is opportune. The fact that a large number of specialists have contributed articles, each one, of course, in the field to which he has given particular attention, ensures critical treatment. It might have been better to have made the book in several volumes to be sold separately, so that each purchaser could secure the part in which he or she is interested. Chemistry is now broken into so many specialties that a comprehensive work of this kind contains much that is of no interest to a particular worker.

Editing does not consist in merely choosing collaborators and reading proof; definite methods of spelling, syntax and form should be laid down. In the work in hand these rules have not been fully observed. References are in some articles quoted by year and volume, in others, by volume alone. The year should always be given. HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS: Report No. 128, Aeronautic Instruments IV—Direction Instruments in Four Parts. By the Aeronautic Instruments Section, Bureau of Standards. 67 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report, in four parts, covers the general field of direction instruments.

Part I points out the adequacy of a consideration of the steady state of gyroscopic motion as a basis for the discussion of displacements of a gyroscope mounted on an airplane, and develops the simple theory on this basis.

The principal types of gyroscopic inclinometers and stabilizers are briefly described and performance requirements stated.

Part II deals briefly with the testing and use of magnetic compasses for airplanes.

Part III contains a brief general treatment of the important features of construction of aircraft compasses, and descriptions of the principal types used in America and in foreign countries.

Part IV gives a brief history of the development of airplane turn indicators, with detailed descriptions of all known types and makes. The results of laboratory and flight tests are given for the several available gyroscopic turn indicators.

Report No. 146, The Six-component Wind Balance. By A. F. Zahm. 12 pages, illustrations, plates, quarto. Washington, Government Printing Office, 1922.

Report No. 146 is a description of the six-component wind-tunnel balance in use at the Aerodynamic Laboratory, Washington Navy Yard.

The description of the balance gives the mechanical details and the method of operation, and is accompanied by line drawings showing the construction of the balance. The balance is of particular interest, as it allows the model to be set up quickly and accurately in roll, pitch, and yaw, without stopping the wind. It is possible to measure automatically, directly, and independently the drag, side drag, and lift; also the rolling, pitching, and yawing moments. The balance can also be made self-recording.

PUBLICATIONS RECEIVED.

Space-Time-Matter, by Hermann Weyl. Translated from the German by Henry L. Brose. 330 pages, illustrations, 8vo. New York, E. P. Dutton and Company, no date. Price $7.50

Molecular Diffraction of Light, by C. V. Raman, Palit Professor of Physics in the Calcutta University. 103 pages, 8vo. Calcutta, University of Calcutta, 1922.

Select Methods of Chemical Analysis. A manual of analytical methods and general reference for the analytical chemist and for the advanced student. Edited by Wilfred W. Scott, Associate Professor of Chemistry, Colorado School of Mines. Third edition, thoroughly revised and greatly enlarged. Two vols., illustrations, colored plates, 8vo. New York, D. Van Nostrand Company, 1922. Price $10.

The Chemistry of Combustion, by J. Newton Friend. 107 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1922. Price $1.25.

Liquid Fuel and Its Apparatus, by Wm. H. Booth. Second edition. 308 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, no date. Price $4.00.

U. S. Bureau of Mines: Bulletin 199, Experimental Production of Alloy Steels, by H. W. Gillett and E. L. Mack. 81 pages, plates, 8vo. Washington, Government, 1922.

National Advisory Committee for Aeronautics: Techanical Notes No. 108, The Use of Multiplied Pressures for Automatic Altitude Adjustments, by Stanwood W. Sparrow. 8 pages, illustrations, quarto. No. 109, The Twisted Wing with Elliptic Plan Form, by Max M. Munk. 7 pages, quarto. No. 111, Stresses Produced on an Airship Flying through Gusty Air, by Max M. Munk. 5 pages, quarto. Washington, Committee, 1922.

Crankless Engines (Aus.), Proprietary Limited, Handbook of the Crankless Engine. 37 pages, illustrations, plates, quarto. Melbourne, Australia, 1922.

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